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PASSIVE SAMPLING DEVICE FOR AMBIENT AIR AND PERSONAL MONITORING

by

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Salient design features of the dosimeter included the following: (1) rugged, simple design and cost effective; (2) small size and simple operation; (3) high equivalent pump rate and high sensitivity; (4) multicomponent sampling capacity; (5) ability to be reused and recharged; and (6) amenability to thermal desorption.

The results of laboratory and field evaluation studies of dosimeter performance are discussed in terms of the design criteria employed in the development of the device and its application to widely divergent sampling assignments. Detection sensitivity at the sub-ppb level was demonstrated for short exposure times (e.g., one hour) employing thermal desorption and halogen specific Hall detector/gas chromatography. Long-term exposures were conducted under ambient air (ppb range) and work station (ppm range) environmental conditions. Retention time windows and detector response factors for 24 halogenated compounds have been established for our computer program to increase compound recognition capability to nonhalogen compounds of current environmental interest.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an indepth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement system, and supplying technical support to other groups in the Agency, including Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of human exposure to toxic organic compounds is an area of increasing importance to EPA. The passive personal monitor described in this study was designed, fabricated, and evaluated by Monsanto Company. This device is a possible candidate to be used in future exposure monitoring studies for volatile organic compounds in ambient air. The commercially available passive sampling devices are used primarily for industrial hygiene purposes where concentrations are orders of magnitude higher than in ambient air. The main goal of the program was to develop a passive sampling device based on thermal desorption that would achieve ppb sensitivity needed for ambient exposure monitoring.

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ABSTRACT

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SECTION 1

INTRODUCTION

A preference is clearly evident for passive dosimeters that meet the rapidly expanding needs of personal and area monitoring. When applicable, these devices offer the capability of detecting multi-component vapors and are low-cost, lightweight, and convenient units.

Passive sampling can be advanced significantly through the timely development of improved sampling devices that are amenable to ambient air as well as personal monitoring applications. Of particular interest are devices providing multi-vapor capability, sensitivity to ppb levels, and convenience, simplicity, and reliability of use.

The first need arises from the large number of chemicals which are likely to be of concern from a public health point of view. The second need is important because low levels of these compounds must generally be considered for ambient sampling applications. The third item relates to the characteristics contributing to the cost-effectiveness, ease of operation, and confidence in the data collected by the passive device.

Properly designed passive dosimeters containing selected polymeric adsorbents can provide highly attractive performance with respect to multivapor capability and sensitivity to ppb levels. A critical need, not yet met by any such device, is the capability for high sensitivity required for ambient air and short-term personal monitoring applications.

The objective of this program was to design, develop and evaluate a prototype passive personal dosimeter based on diffusion principles and employing porous polymer sorbents that will meet all of the performance requirements stated above. The personal dosimeter was to be capable of monitoring the following toxic organic pollutants at the part-per-billion level in ambient air: benzene, vinyl chloride, trichloroethylene, tetrachloroethylene, chloroform, carbon tetrachloride, chlorobenzene, dichlorobenzene, 1,2-dichloroethane, and trichloroethane.

The personal monitor design was to be similar in size to a radiation badge so that it could be easily worn. The sorbent materials in the badge were to be chosen so that a wide range of toxic

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organic pollutants could be monitored, or if more selective monitoring was desired, sorbents could be chosen to preferentially collect specific compounds. The units were to be designed and developed in a manner that would maximize models.

Laboratory tests and evaluations of the approved prototype were to be conducted to determine overall performance. These efforts were to include the unit's efficiency in the collection and analysis of the President's Public Health Initiative pollutants. Testing was to include determination of sensitivity limits, selectivity, shelf life, artifact formation, and other salient characteristics.

In the device developed in this program, sampling is completed on a time-weighted basis, whereby organics of interest are quantitatively collected onto the sorbent bed, recovered by thermal desorption, and subsequently analyzed by standard gas chromatographic (GC) techniques utilizing specific GC standards.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

A high performance passive dosimeter was developed to meet the rapidly expanding needs of ambient air and short-term, low-level, personal monitoring. This device, employing a porous polymer as the sorbent medium, satisfies the strigent requirements imposed by ambient air sampling. Detection sensitivities in the part-per-trillion (ppt) to part-per-billion (ppb) range have been demonstrated for seven halogenated organic compounds at exposure times of about one hour. Retention time and detector response data for twenty-four halogenated compounds were developed to extend compound recognition capabilities. This simple, inexpensive monitor demonstrates multicomponent sampling capabilities. Sampling performance of the passive device is comparable to active "pumped" sampling tubes. Device performance is provided by the equivalent pump rate characteristics, the high sample recovery via a thermal desorption process, and the detection sensitivity and specificity afforded by multiple specific detector GC analysis.

While in-depth laboratory and field evaluation studies have been conducted with the monitor, more comprehensive field studies should be completed to demonstrate the practical applicability of the monitor to real sampling problems. Hazardous waste sites represent a timely sampling problem that would provide a good practical evaluation of the monitor.

SECTION 3

PASSIVE DOSIMETER DESIGN CONSIDERATIONS

Application of the passive dosimeter approach to specific sampling problems involves three principal areas of technology: diffusion considerations, sorbent selection, and chemical quantitation of the sampled compounds which intimately involves desorption of adsorbed materials from the passive device. Figure 1 illustrates schematically the steps involved in using passive dosimetry.

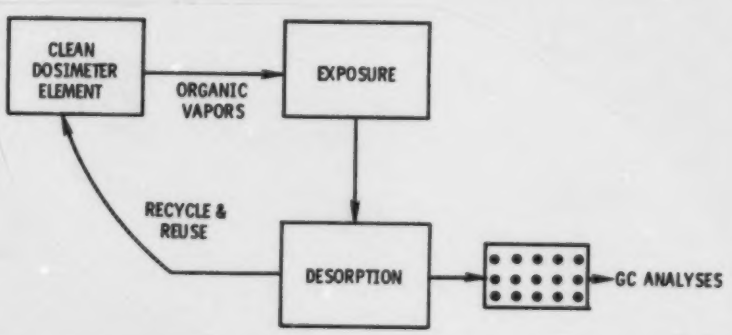


Figure 1. Steps involved in using passive dosimetry.

DIFFUSION CONSIDERATIONS

Passive devices measure time-average concentrations by collecting the vapor present in the surrounding air according to well-defined physical principles of diffusion mass transport. Aerosol and particulate-sorbent materials are not measured; therefore, the devices provide information on vapor concentration directly. No pumps or power supplies are required.

The mass transport of a chemical present in the air to the adsorbing element of a passive dosimeter can be expressed by Fick's first law of diffusion:

$$J = -D(\partial C/\partial X) \qquad (1)$$

J is the flux of the diffusing substance, expressed as mass per unit of surface area normal to the diffusion path per unit time. D is the diffusion constant for the substance of interest; it is a physical quantity expressed in units of length^2/time and is

reported in the literature for many materials. When experimental data are unavailable, D can be calculated with some degree of accuracy. C (mass/volume) is the local concentration of the diffusing substance expressed at any point X (length) along the diffusion path. The partial derivative in Equation 1 indicates that a change in concentration must occur along the diffusion path in order to sustain mass transport, and the negative sign indicates that the concentration must decrease in the direction of diffusion.

Equation 1 applies to the "steady state" situation in which, after an initial period of establishing equilibrium, the diffusion system assumes a state where J and $\partial C/\partial X$ remain constant with time. Under these conditions, mass can be considered to diffuse "downhill" from a steady supply (fixed concentrations) in the outside air to a stable sink (concentration essentially zero) inside the dosimeter.

The strict one-dimensional application of Equation 1 may be illustrated as follows. Suppose that the dosimeter is a simple box of depth ℓ, with the front face formed by a screen and the back face by an effective sorbent for the gas of interest (see Figure 2). Suppose also that the constant gas concentration C_0 of a substance is maintained in the air adjacent to the wire screen, while a gas concentration of essentially zero is maintained at the sorbent face (due to the sorbent's affinity for gas molecules impinging on it), and that the region between the faces of the box is stagnant and free of the convection currents normally present outside the box. Under these conditions, the flux J is constant with time; the concentration gradient $\partial C/\partial X$ also is constant and therefore defines the one-dimensional concentration profile $C = C_0 - (C_0/\ell)X$. This linear change in C inside the box with distance X is illustrated by the dashed-line in the graph superimposed on the dosimeter of Figure 2.

The exact profile of $\partial C/\partial X$ within a given dosimeter may be quite complicated, however, owing to dosimeter geometry, convection currents, dependence of D on concentration, and other factors. Indeed, in most practical cases, a two- or three-dimensional version of Equation 1 would be required to describe the process. Nevertheless, Equation 1 provides an adequate basis for assessing the role of dosimeter design parameters on performance.

The relative influence of dosimeter design parameters also may be illustrated with the device of Figure 2, which is closely approximated in general features by some commercial dosimeters. The two quantities of most interest are the mass transport rate of the dosimeter and its dynamic range in accommodating values of the time-integrating quantity Ct, from the lowest to the highest values likely to be encountered in actual sampling experience.

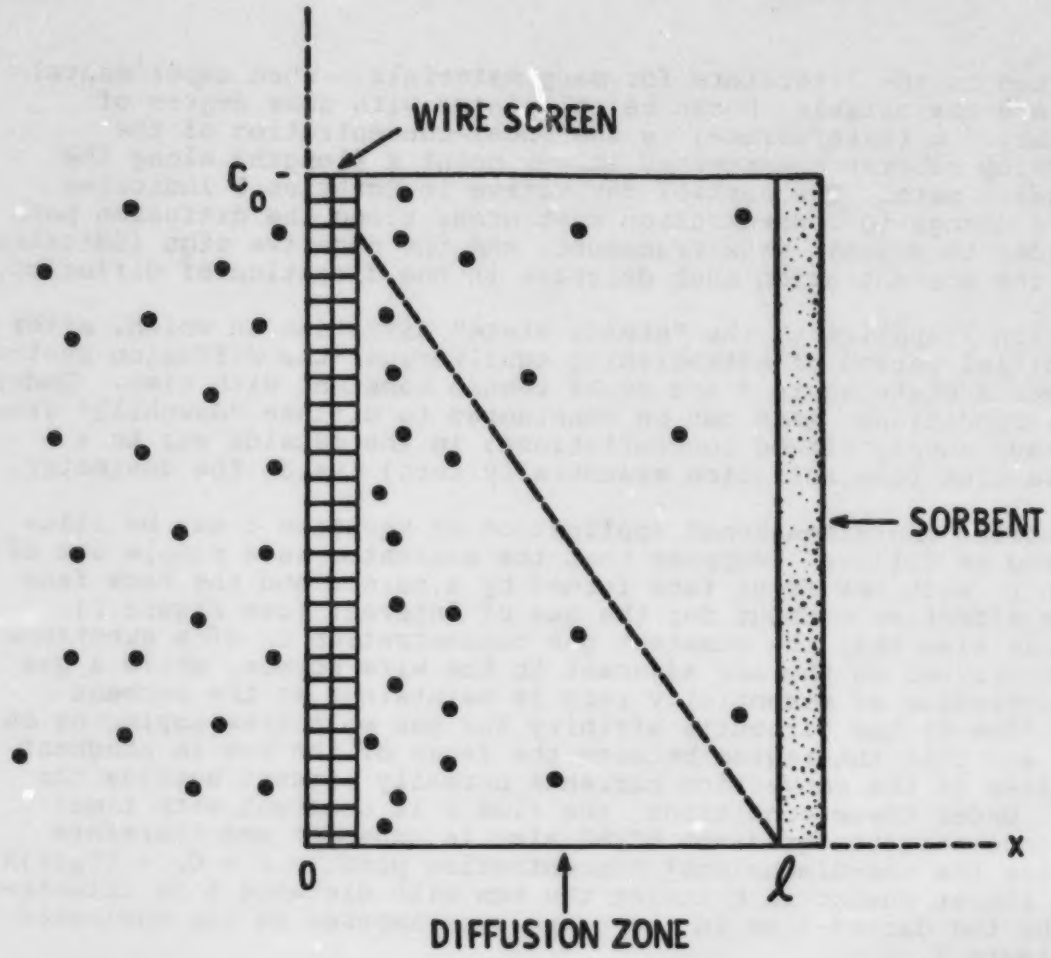


Figure 2. Schematic representation of rectangular dosimeter with one-dimensional diffusion pattern. (Concentrations of diffusing substance at various locations inside the device are indicated by dash-line overlay.)

The mass transport rate of a dosimeter is directly related to its ability to collect low-level concentrations C or, more accurately, to obtain measurable pollutant masses on the sorbent medium for the smallest possible values of Ct (i.e., concentration x time). It may be useful to express a quantity termed the "equivalent air flow" (EAF) which will permit direct comparison of the pollutant collection rate with that of a sampling pump/sorbent tube system.

A sampling pump, operating at a pumping rate Q_v (cm^3/s) in ambient air having a concentration of (g/cm^3) of a given pollutant, will deliver a pollutant mass collection rate of Q_vC (g/s) to a sorbent.

The corresponding expression for the collection rate of a passive dosimeter is the product JA (g/s), where A is the area through which diffusive mass flow into the dosimeter occurs.

$$JA = -DA\,(\partial C/\partial X) \qquad (2)$$

Equating the two collection rates shows

$$Q_v = -(DA/C)(\partial C/\partial X) \qquad (3)$$

or, in the one-dimensional example where $\partial C/\partial X = -C_0/\ell$

$$Q_V = DA/\ell \qquad (4)$$

Equation 4 shows that in order for a passive dosimeter of the Figure 2 design to collect the same quantity of a gaseous pollutant per unit time as a pumped sampler deposits on its absorbent, the volume flow rate of the latter must be numerically equated to the quotient DA/ℓ. Note that the comparison does not involve the magnitude of C. Thus, all contributions of D, A, and ℓ meeting the required equality may be considered and apply equally at low or high sampling concentrations. Because D is a constant by nature (typically about 0.05 to 0.1 cm^2/s), the practical choices reduce to the dosimeter geometry and the associated dimensions.

Passive dosimeters can be designed for operation in various time and concentration regimes for different applications. At the start of this program, the sampling of ambient air (for example, one part per billion) in one hour was assumed as the goal of the MRC passive dosimeter design.

SORBENT SELECTION

In addition to diffusion law considerations, dosimeter performance characteristics also are greatly influenced by the judicious selection of polymeric adsorbents used in the passive device. The key to the selection of the sorbent material lies in the ability of the sorbent to hold the compound(s) of interest at the sampling conditions and then readily release the compound(s) at the desorption conditions with minimum background interference. The ideal situation occurs when the sample is completely and irreversibly sorbed at the sampling conditions. This can be accomplished in certain types of specific chemical interactions (e.g., formation of organometallic complexes), but the reverse process (i.e., desorption) may not be readily achievable in many cases.

When a porous polymer sorbent is used, sorption is not complete and irreversible; rather, an equilibrium is established between the sample on the sorbent surface and that in the vapor state. Such sorbent materials should be selected so that this equilibrium lies strongly in the direction sample collection on the sorbent surface at the sampling conditions. This selection should be

based on the sorption characteristics of a broad range of compounds to achieve the generalized sorption capability for a multicomponent dosimeter. If more selective sampling is desired, sorbents can be chosen and/or modified to preferentially collect particular compound types through specific but reversible interactions. It also is possible to combine sorbent materials to achieve the desired range of sorption capability.

CHEMICAL QUANTIFICATION OF EXPOSED PASSIVE DOSIMETERS

Chemical quantification of exposed passive dosimeters entails a two-step procedure. The first step involves the removal (desorption) of collected compound(s) from the sorbent material in a matrix compatible with appropriate analytical methodology. The second step is the determinative procedure itself, which in this case is a gas chromatographic (GC) procedure.

Thermal Desorption

A strong feature of passive dosimeters employing heat-stable porous polymer sorbents is the ability of the sorbent to be thermally desorbed onto a chromatographic column and the feasibility of analyzing the collected compounds by straightforward chromatographic techniques. The desorption time can be made very short with proper design of the dosimeter, this can circumvent, in many cases, problems associated with solvent extraction. High sensitivity results from a thermal desorption approach because no dilution steps are involved. In some instances, however, thermal desorption is inappropriate and solvent extraction must be employed. With solvent extraction, the resulting sample solution may be analyzed many times, if desired, in order to test improvements in the analytical method, verify results, or simply repeat an analysis in which a mistake was made. Furthermore, many automated sample introduction devices are available for liquid samples, so that many analyses can be performed quickly or conveniently overnight. Unfortunately, solvent desorption reduces the analytical sensitivity greatly by diluting the concentrated sample with solvent. For example, by desorbing the components from a sorbent into 5 mL of solvent, only 1/5,000 of the total sample is analyzed with a 1-μL injection of the sample solution. Results obtained could theoretically be enhanced 5,000-fold by thermal desorption. In cases where solvent extraction is mandated, high sampling performance depends on the dosimeter providing sufficient sample for low concentration detection at short sampling intervals.

Specific Detector-GC Analysis

Overall performance is further enhanced by the utilization of advanced chromatographic techniques for quantitation of the exposed passive device. Packed and capillary column approaches are both

appropriate for providing the isolation for "clean" compound separation. The nonspecificity of conventional GC analysis has traditionally been a major drawback of the technique. This has led to the heavy dependence on gas chromatography/mass spectrometry (GC/MS) as the technique for accomplishing unequivocal identification of compounds. Employment of specific and semi-specific GC detectors (e.g., photoionization, and N-, P-, and S-specific flame ionization), however, offer degrees of selectivity for certain compounds that have the potential for decreasing the dependence on GC/MS. The simultaneous operation of a number of these detectors during an analysis permits the comparison of different detector responses for compounds "seen" by more than one detector. When used in conjunction with GC retention times, detector response ratios provide an additional parameter that greatly improves the confidence of compound specificity of GC analysis.

SECTION 4

EXPERIMENTAL PROGRAM

HARDWARE AND ANALYTICAL METHODOLOGY

High Performance Passive Dosimeter Design

A high-performance passive dosimeter design was developed in this program for evaluation as a monitor for volatile organics in ambient air and short-term, low-level, personal monitoring applications. Design considerations discussed in the previous section were employed to advance this test design which is characterized by:

- Rugged simple design
- Inexpensive, easy operation
- Small size
- High equivalent pump rate
- Multicomponent capability
- Ability to be reused and recharged
- Ability to be thermally desorbed readily

Although laboratory and field performance evaluation studies in this program were conducted using volatile chlorinated organic compounds, the resulting dosimeter design is not limited to this compound class but can be extended to a broad spectrum of compounds through sorbent selection and appropriate analytical procedures.

Unlike commercially available dosimeters, the Monsanto Research Corporation passive dosimeter design shown in Figure 3 is of stainless steel construction. This material of construction was selected for three reasons. First, all-metal construction makes the device amenable to thermal desorption, which substantially contributes to the high overall detection sensitivity required for ambient sampling. Secondly, metal construction helps eliminate the possible sinks and/or sources problems for volatile organics associated with some plastic materials. Thirdly, such construction leads to a rugged device that can withstand not only the rigors of a single sampling assignment and be reused many times, thus leading to a very cost-effective device.

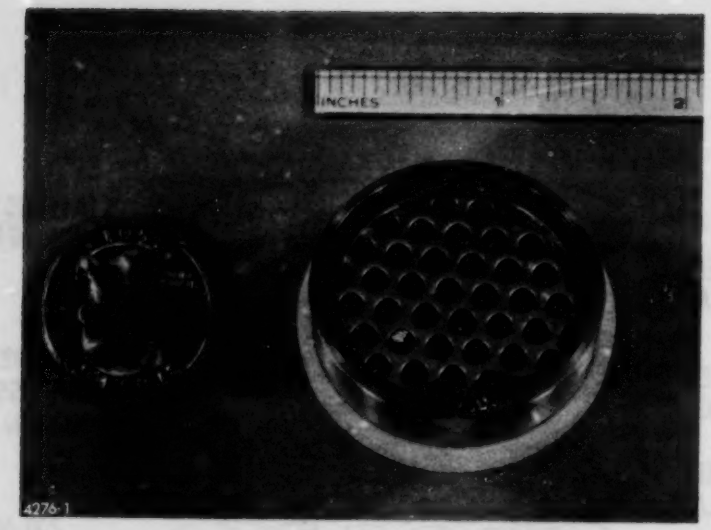


Figure 3. Assembled dosimeter shown in sampling mode.

Basically, the dosimeter (Figures 3 through 5) consists of a stainless steel body, 1-1/2 in. in diameter and 7/16 in. high. The internal diameter of the body is 1-3/8 in. with the exception of the central portion, which is reduced to 1-3/16 in. ID to provide a precise defined containment volume for the porous polymer. Stainless steel screens and perforated plates serve to confine the polymer within the dosimeter body and provide diffusion barriers. A 200-mesh square wire cloth (Cleveland Wire Cloth and Manufacturing Company) with 33.6% open area is used for the diffusion screens. Backup plates are punched from stainless steel perforated stock having 0.040-in. diameter holes in a straight line center pattern, 225 holes/in.^{2} and 28% open area. Four screens and perforated plates are used in each dosimeter and arranged in a symmetrical configuration. Dosimeter assembly begins with the placement of a screen and backup plate in the dosimeter, seated on the shoulder of the center body web. A friction snap ring is used to hold the screen and plate tightly against the web shoulder. This describes a volume to contain the solid sorbent. Once a measured amount (~0.4 g) of sorbent is placed in the dosimeter, a screen and perforated plate are placed over the sorbent and seated on the web shoulder. Additional screen-plate-retainer rings are added to both faces of the dosimeter to complete the diffusion zone. The dosimeter is easily assembled, and it can be easily disassembled to replace or change the sorbent.

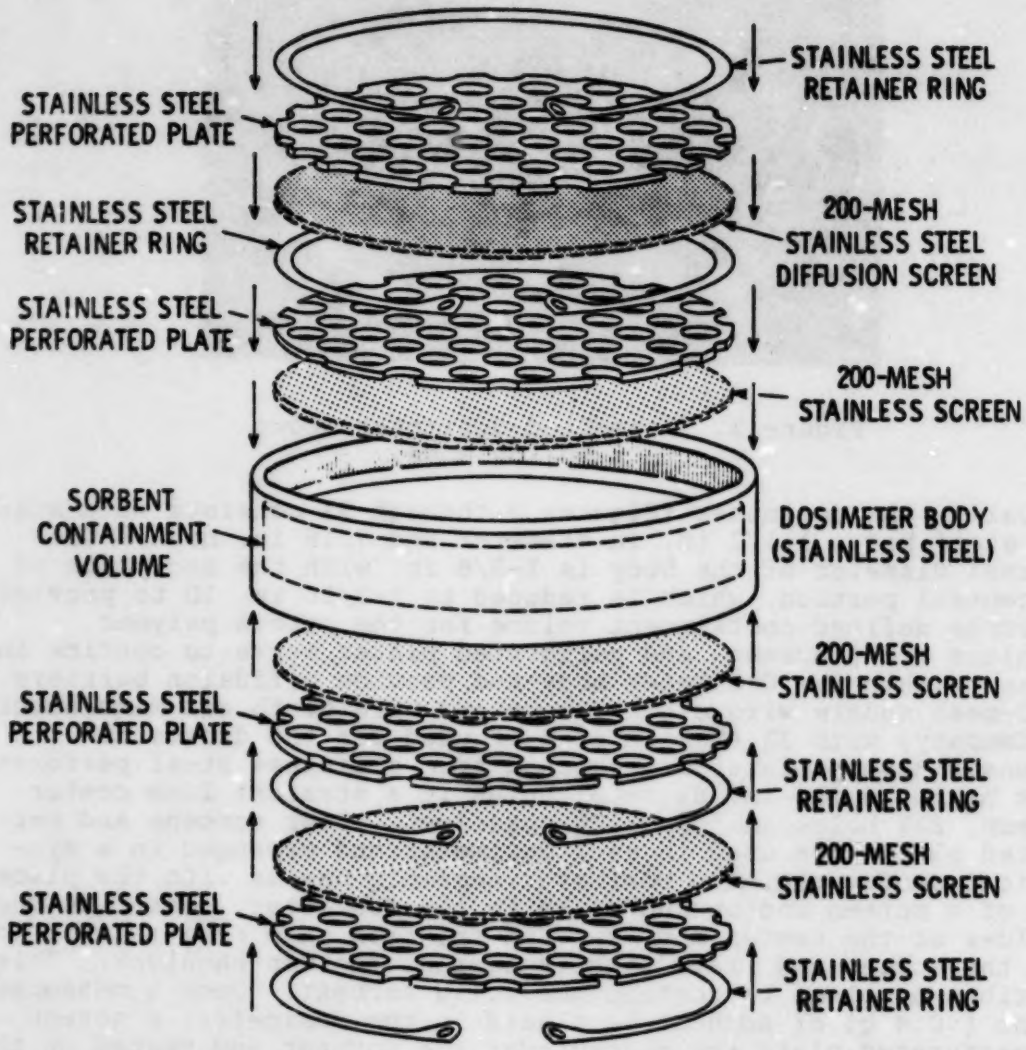


Figure 4. Passive dosimeter for laboratory prefield testing and evaluation.

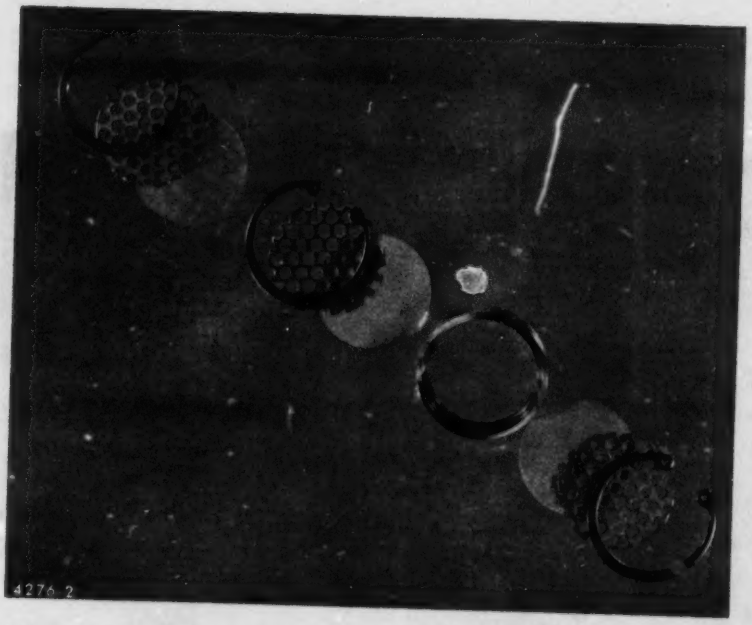
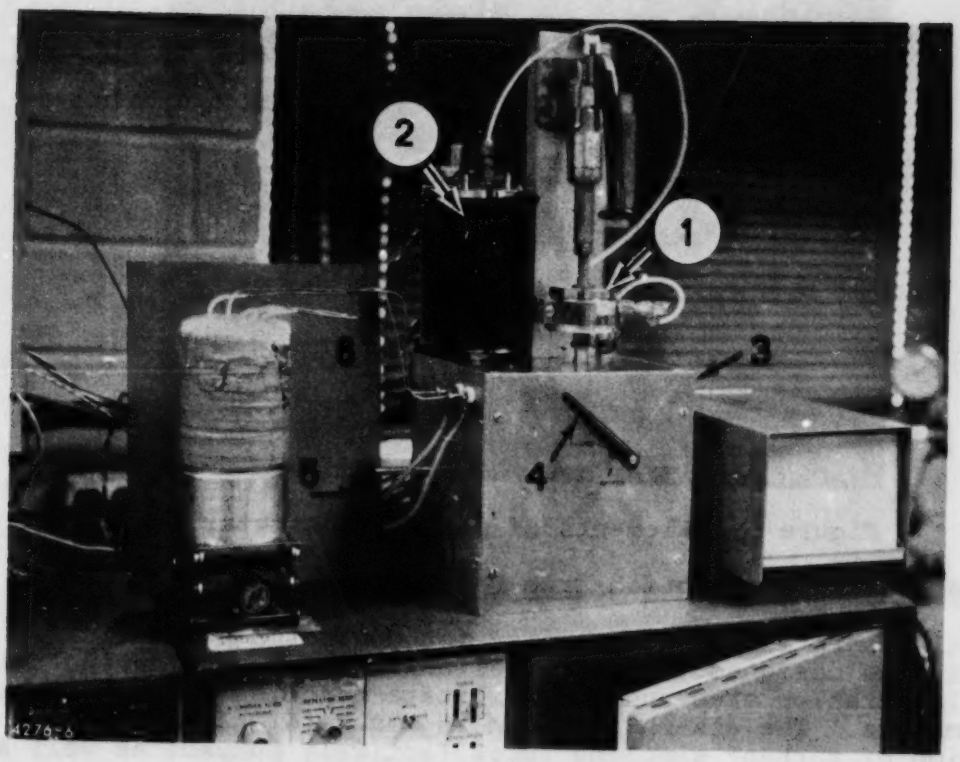


Figure 5. Elements of passive dosimeter.

Dosimeter Thermal Desorption/Trap Unit

A thermal desorption oven, required for dosimeter desorption/analysis, was designed to ensure reliable performance during this critical operation step and to facilitate handling a large number of dosimeters. The assembly, shown in Figure 6, handles the desorption of sorbent sampling tubes (actively pumped) as well as the passive dosimeters. The unit is composed of two manually operated six-port, high-temperature (300°C max.) Valvo® valves. "Switching valve" No. 1 (Figure 7) directs helium purge gas through either the sorbent tube or the passive dosimeter path to a second valve which selects the "desorb/trap" or "analyze" mode of operation. The "desorb/trap" mode diverts the purge gas through a cryogenically cooled sample loop to provide off-line trapping which in addition provides better carrier-gas flow rate control. When valve No. 2 is switched to the "analyze" mode, a second gas stream (helium carrier-gas) is backflushed through the sample loop which is ballistically heated to transfer the trapped compounds to the analytical column for chromatographic analysis.

The heater control unit shown in Figure 8 provides manual control to five heat zones, two of which can be operated by a timer.



(1) Dosimeter thermal desorption oven
(2) Sorbent sampling tube desorption oven
(3) Insulated valve housing
(4) Desorb-analyze mode valve
(5) Dosimeter-tube selector valve
(6) Ballistically heated trap

Figure 6. Dosimeter thermal desorption/trap unit.

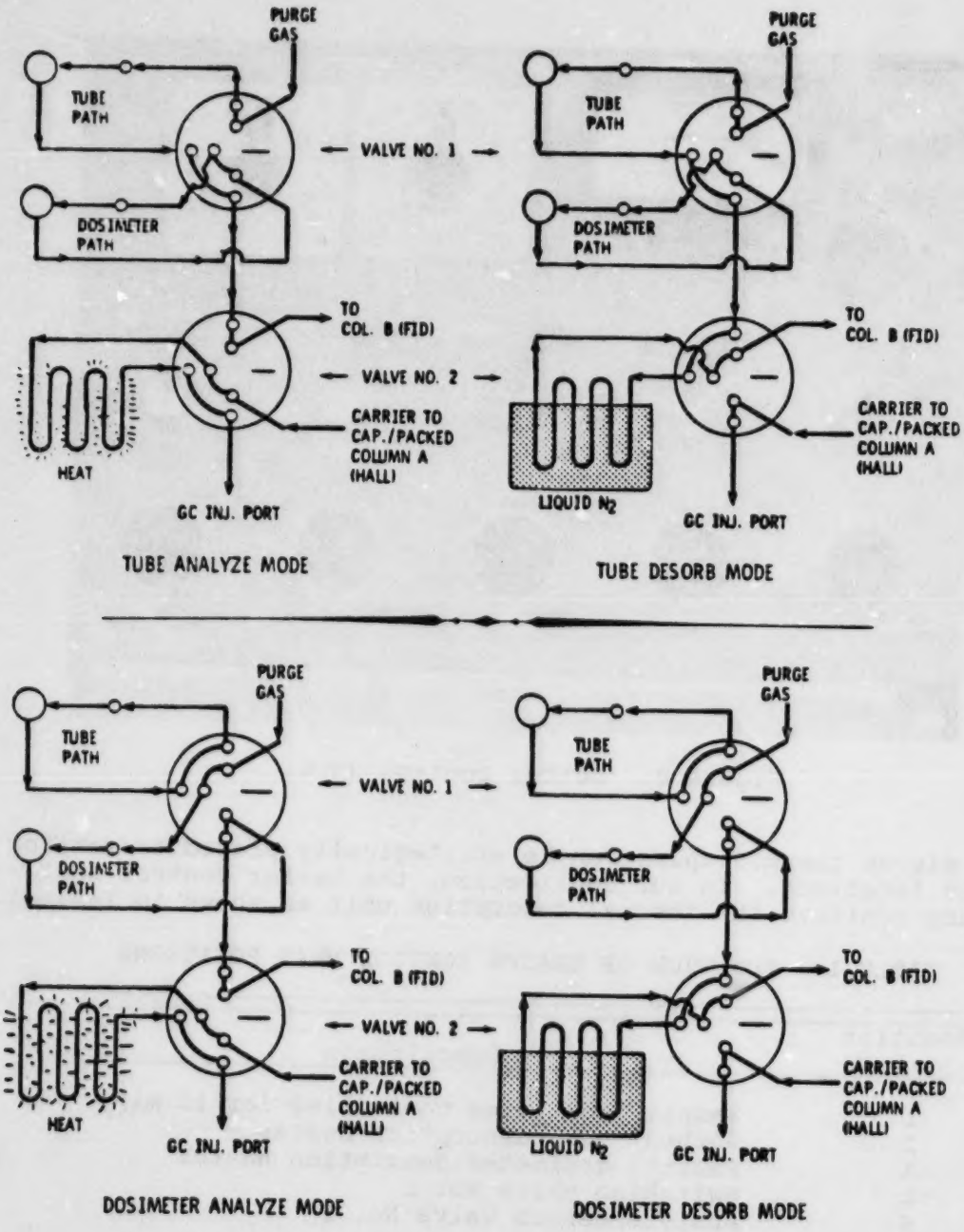


Figure 7. Thermal desorption/trap unit schematic.

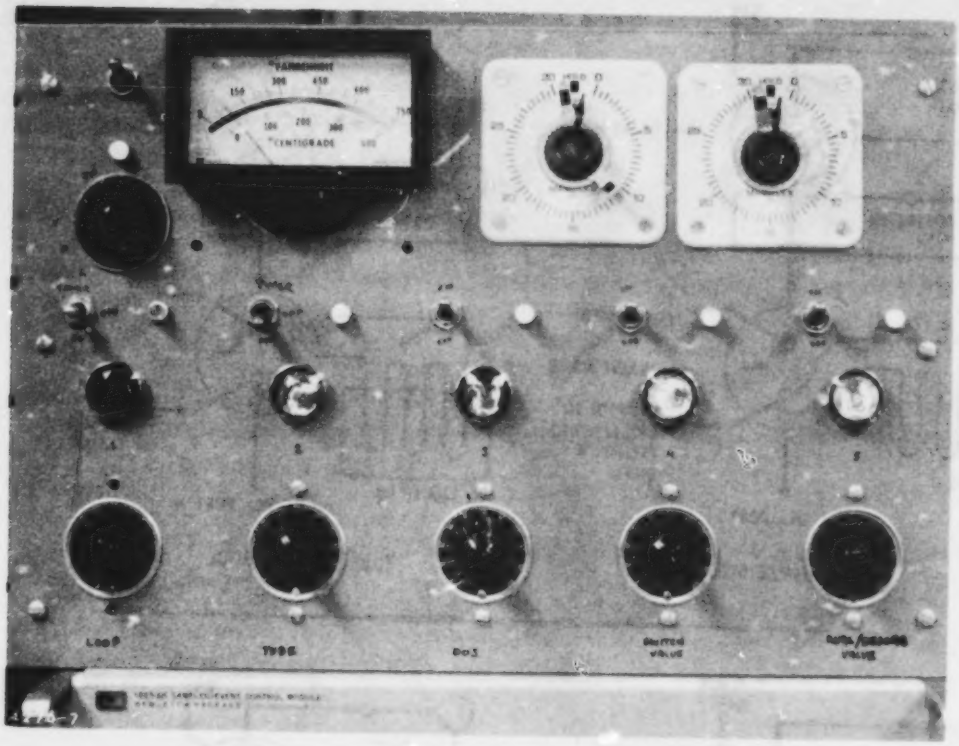


Figure 8. Heater control unit.

Up to eleven thermocouples can be strategically placed to monitor various locations. In our application, the heater control unit sets and monitors the thermal desorption unit as shown in Table 1.

TABLE 1. FUNCTION OF HEATER CONTROL UNIT POSITIONS

Position number	Description
1	Sample loop (time controlled for 10 min)
2	Sorbent tube desorption heater
3	Passive dosimeter desorption heater
4	Switching valve No. 1
5	Analyze/desorb valve No. 2

Chromatographic Program for Dosimeter Analysis

Compound recognition capabilities were included in the chromatographic analytical program to better identify the broad range of chlorinated compounds often collected under field sampling conditions.

Chromatographic conditions employed for the analysis of dosimeters and sorbent sample tubes are given in Table 2. A representative chromatographic program is shown in Figure 9 for halogen detection by the Hall electrolytic conductivity detector (HECD). The GC column effluent is split and sent to both the Hall detector and an HNu photoionization detector (PID) for selective determination of halogens and semi-selective determination of aromatics, respectively (Figure 10).

TABLE 2. GAS CHROMATOGRAPH/HALL ELECTROLYTIC CONDUCTIVITY DETECTOR CONDITIONS FOR DOSIMETER ANALYSES

Instrument:	Chromatograph:	Hewlett-Packard Model 5711
	Hall Detector:	Tracor Model 700 (in chlorine mode)
	Photoionization Detector:	HNu Model P1-52
	Auto Sampler:	Hewlett-Packard Model 7671-A
Column:	8 ft x 2 mm (ID) glass packed with 1% SP1000 on 60/80 mesh Carbopack B	
Temperature Program:	60°C to 210°C at 8°C/min, hold at 210°C for 15 min	

Other Conditions:

Parameter	Temperature, °C
Injection Port	200
Transfer Line	250
Hall Reactor	850
	Flow rate, mL/min
Helium (carrier)	40
Hydrogen (reactor gas)	45
Electrolyte (n-propanol)	0.75

Three different compound mixes were employed to provide greater capability with respect to retention time determination. A total of twenty-four compounds comprised the three standard mixes. Retention time windows was established for our computer program

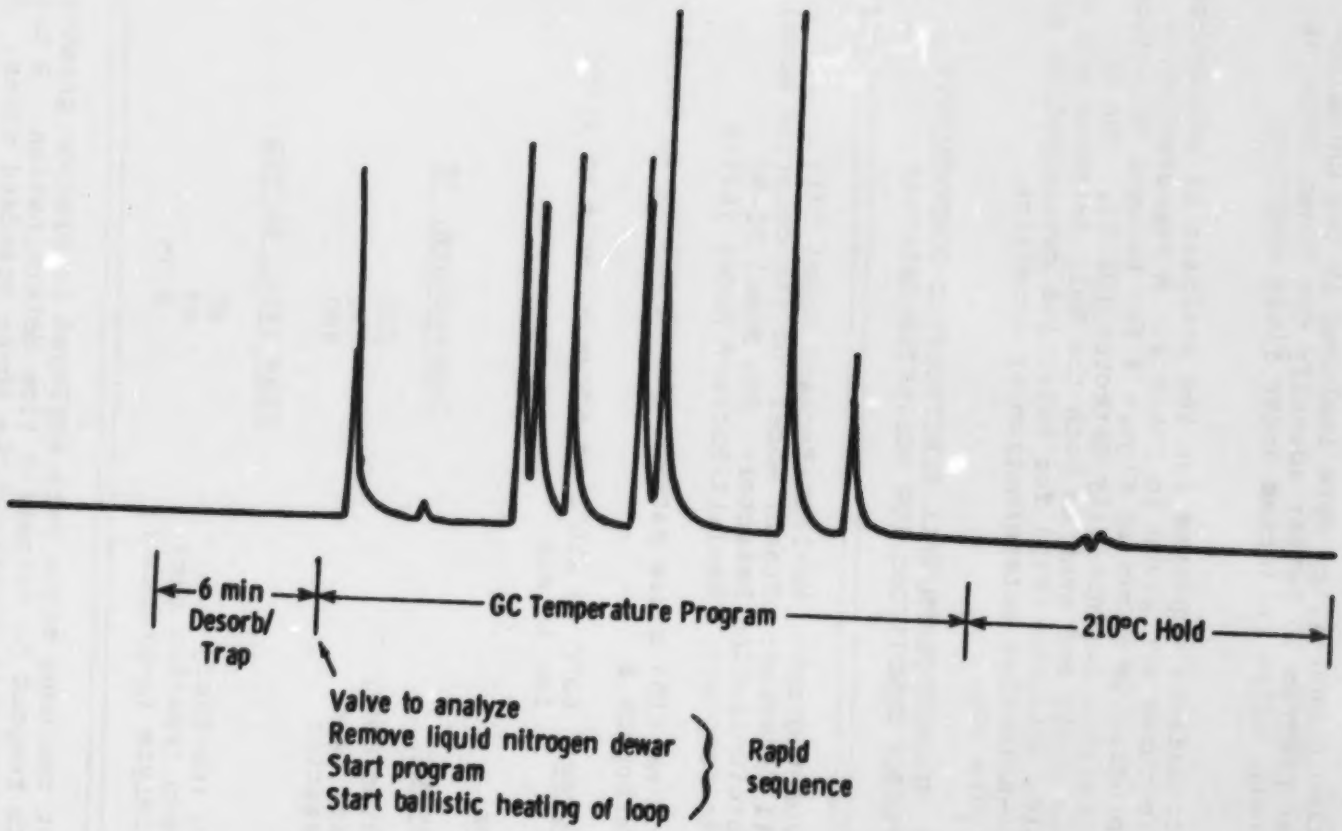


Figure 9. Representative chromatographic program.

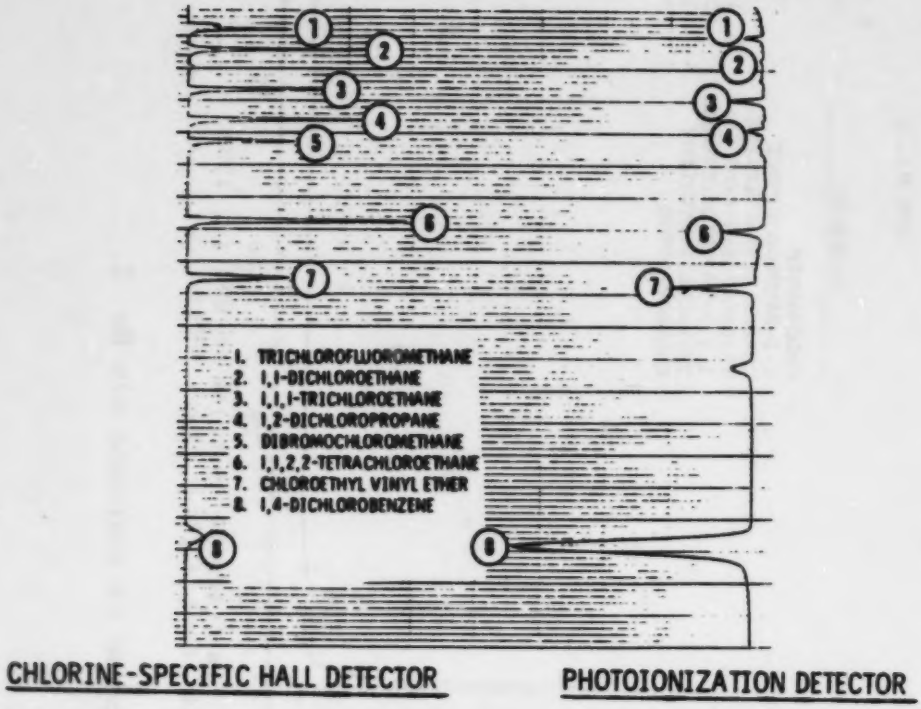


Figure 10. Compound specificity enhancement by use of multiple GC detectors.

along with the necessary detector response factors required for compound identification and quantitation. Compounds comprising the three mixes and their associated reconstructed chromatograms are shown in Figures 11 through 13.

Standards Generation

Standards for this program were prepared by successive dilutions of stock solution. Stock solutions were prepared using either gravimetric or volumetric addition of the solute to a small portion of the solvent, followed by dilution to volume. In addition to liquid standards, gas standards were generated for dosimeter evaluation studies using a sample generation system employing a syringe drive of fluids into heated blocks with three calibrated dilution stages.

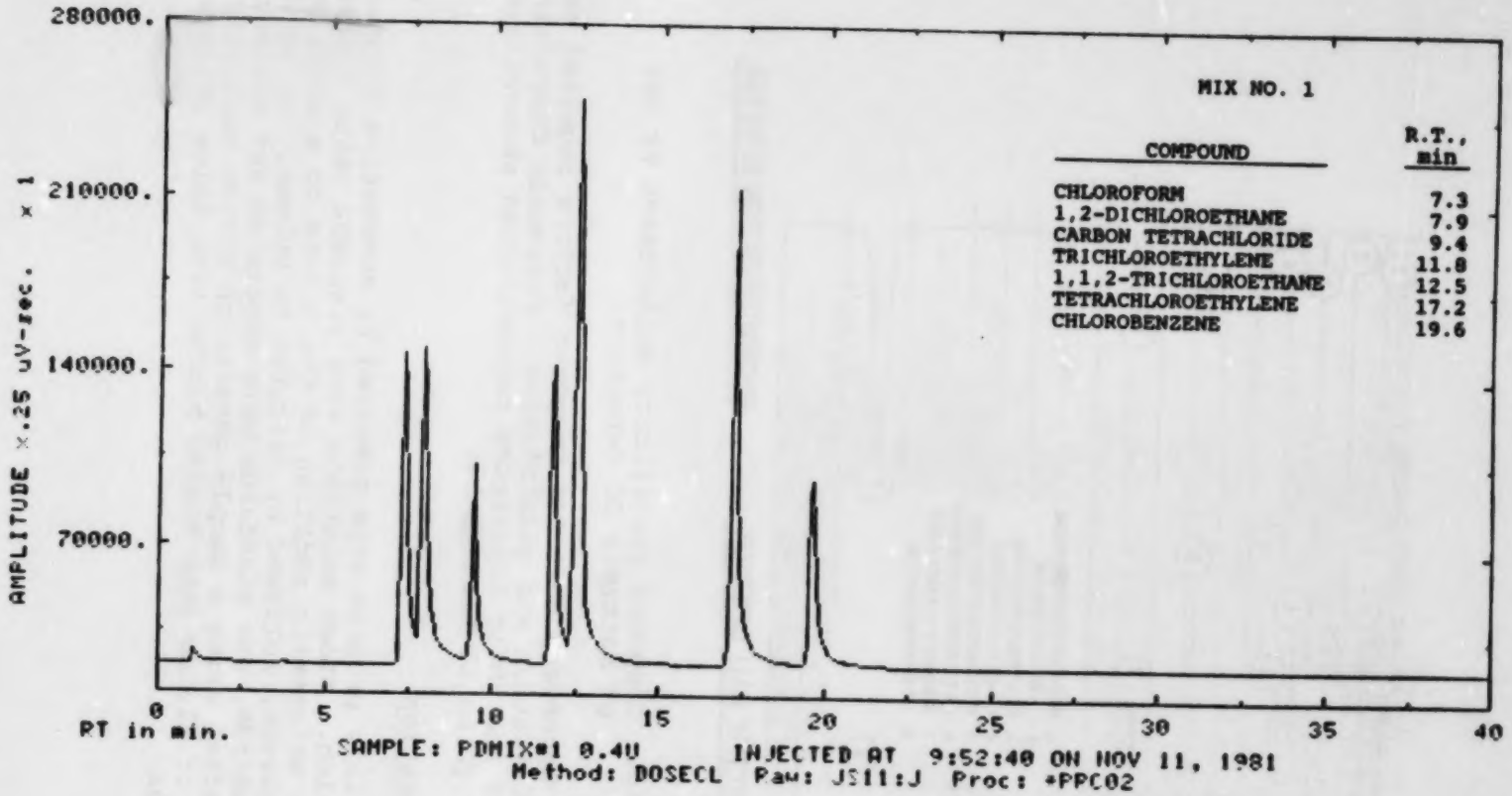


Figure 11. Chromatogram of compound mix No. 1.

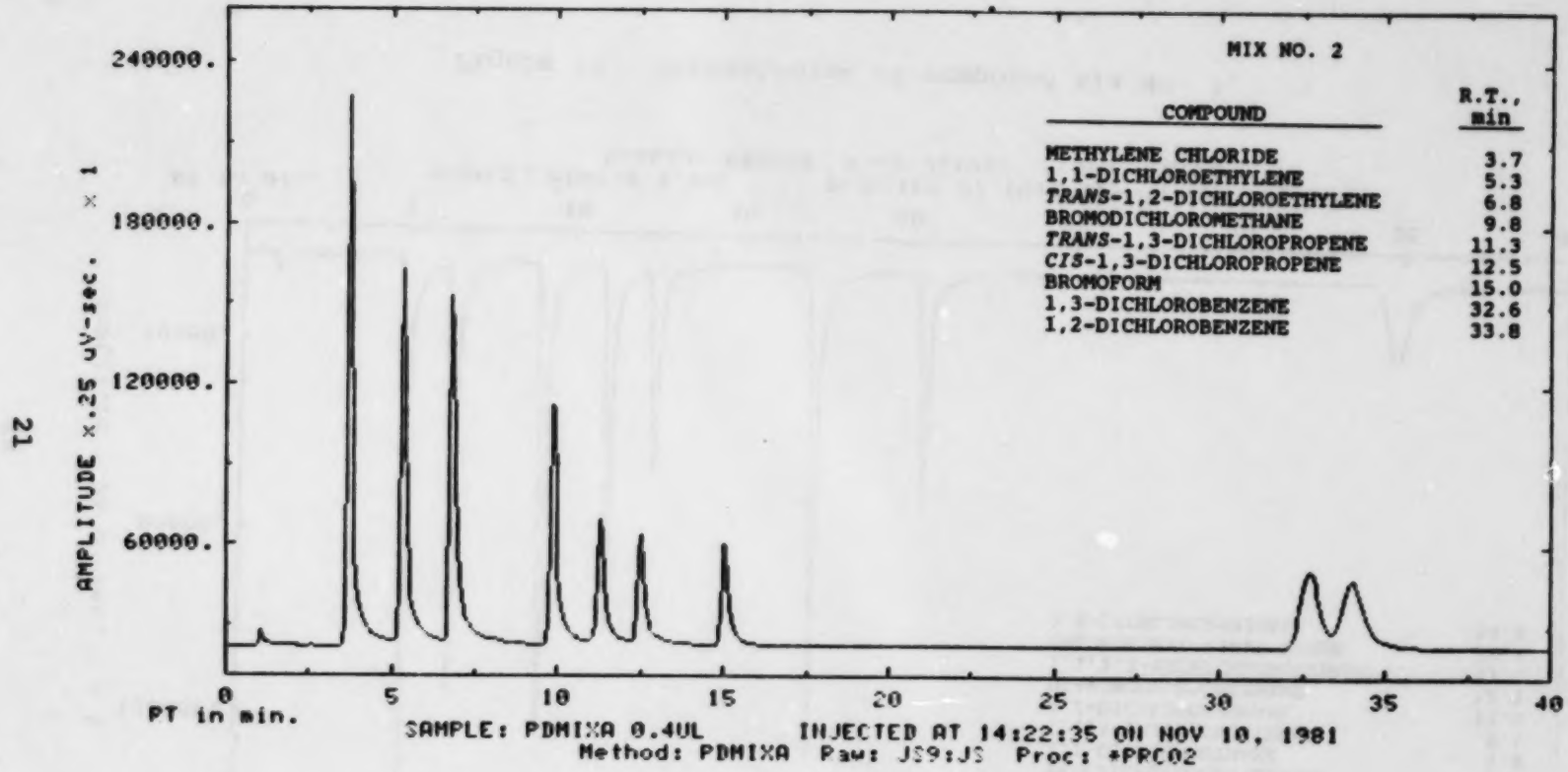


Figure 12. Chromatogram of compound mix No. 2.

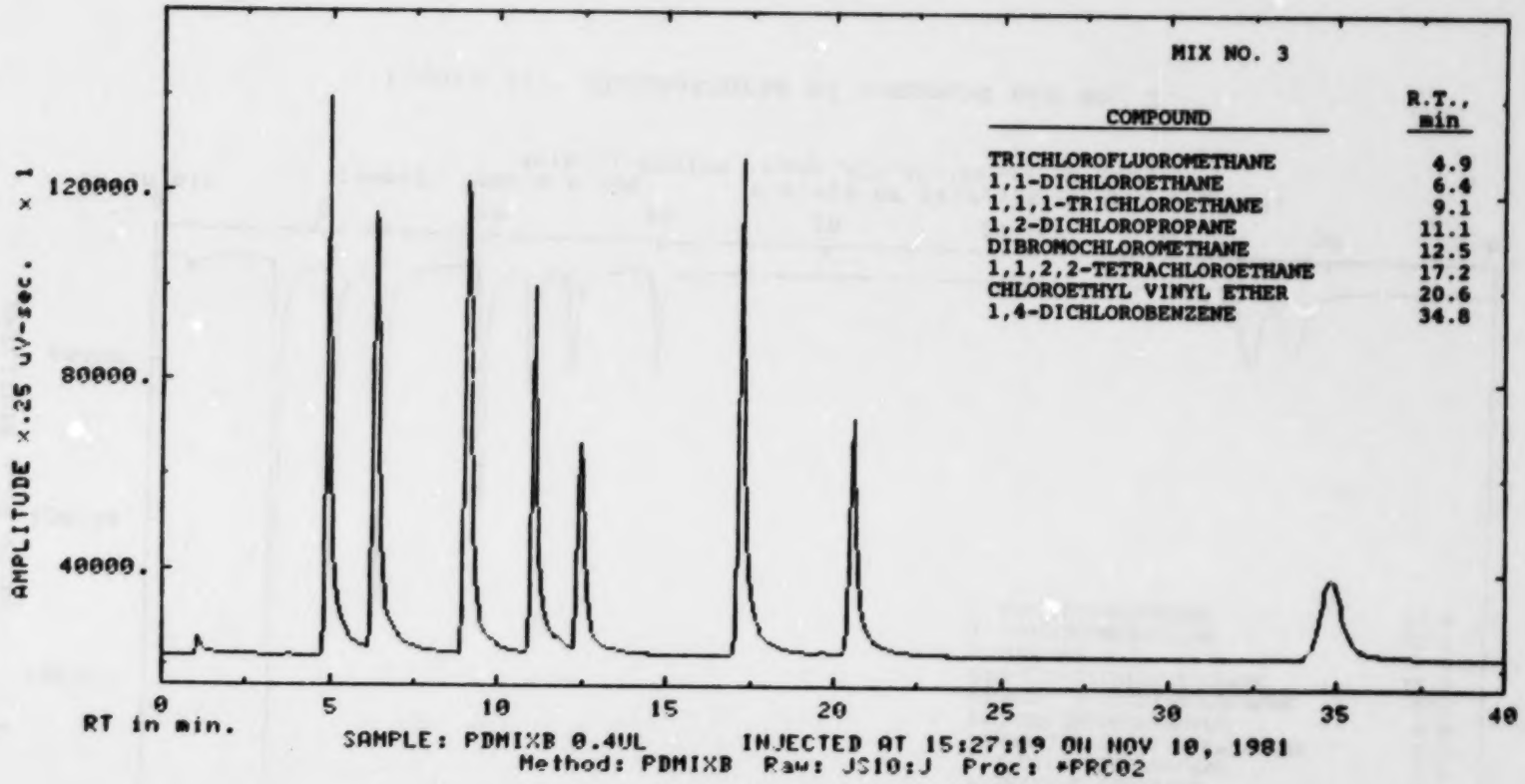


Figure 13. Chromatogram of compound mix No. 3.

The sample generation system shown schematically in Figure 14, included the main frame, which was a modified gas chromatograph with its protective metal covering and detector removed. The oven (30 cm x 30 cm) was located on the left side of the main frame. Of the four heated zones available on the original GC, one controlled the oven temperature, two were used to separately control the temperature of the two three-port injection blocks, and the final zone was available for heating transfer lines used for direct interfacing with a detector in frontal analysis capacity studies. A pyrometer (Simpson 0-500°C), a selection switch, thermocouples, and necessary circuit modifications allowed the monitoring of temperatures in the four zones.

An aluminum plate (45.7 cm x 46.4 cm x 0.6 cm) was attached to the main frame to the right of the oven to accommodate the syringe drives. Necessary bulk-head gauges and rotameters were used in the configuration indicated in the figure. Materials of construction for the flow system were either stainless steel or nickel, and the entire system was contained in a large exhaust hood (2.4 m x 1.2 m x 1.5 m) with front and rear access through double sliding doors. Flow control/sensing instrumentation, pressure gauges, and rotameters were mounted on a panel and rack assembly in the hood above the generation system.

The generation system functioned in the following manner. A source of carrier gas (N_2) was introduced into the system and split into primary, secondary and tertiary flows. The primary flow passed through a mass-flow sensor/controller (Brooks Model 5841) which maintained the flow rate at a preset value (0 to 1,000 mL/min). This flow passed through individually heated and controlled injection blocks which were each designed to accept three syringes mounted on variable-control syringe drives (Sage Model 355). This permitted the simultaneous introduction of six pure liquid components, or potentially many more, if mixtures of compounds were used in the syringes. The rate of injection could be varied from submicroliter/hour to milliliter/minute by the appropriate choice of syringe size and drive rate. Liquid samples were vaporized in the injection blocks and swept with the carrier gas into a constant temperature oven.

Most of the primary flow passed through the oven and through a needle valve used to regulate the pressure in the primary flow path. It was then expelled to the vent (V1). A small portion (usually ~10 mL/min) of the primary flow was removed through a dual-control needle valve and passed into a switching valve (SV1) which was actually one-half of an eight-port switching valve. The second half of the switching valve was used for an identical function in the second dilution stage. The switching valve made it possible to insert a mass-flow sensor (Brooks Model 5810, 0 to 100 mL/min) in the flow path (indicated by the dashed line in Figure 14) to measure the exact split of the primary flow. Once

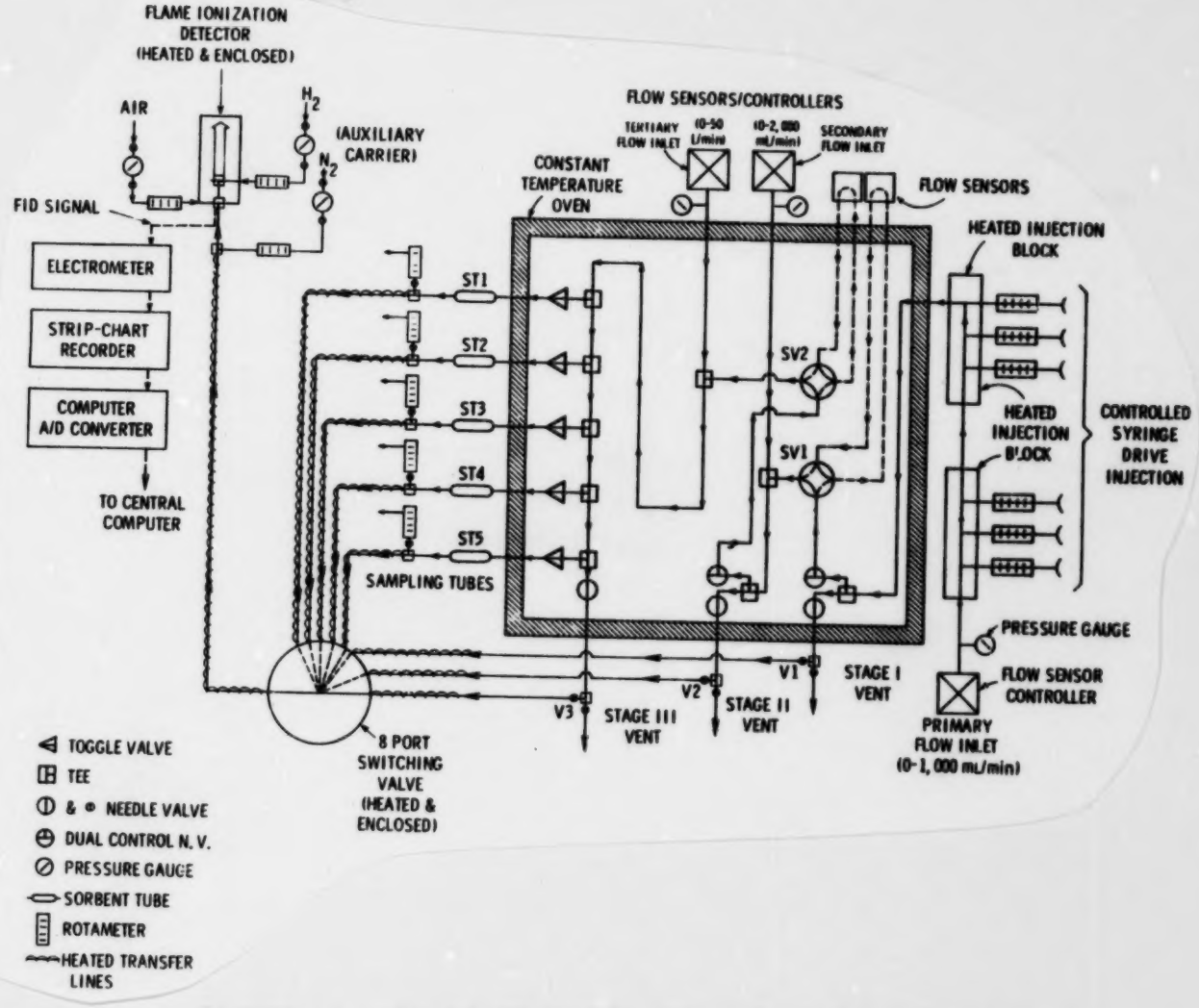


Figure 14. Standard Sample Generation System (SGS) with effluent monitor modification.

the split had been established, the flow sensor was switched out of the system so that the sensing elements were not subjected to sample-containing organic vapors. The split was maintained by carefully controlling the pressures in each dilution stage.

Pressures were monitored with precision pressure gauges [Heise Model CM, 0 to 6.9 x 10^5 Pa (0 to 100 psi)]. By maintaining a constant pressure in each dilution stage, a constant pressure differential was established between the stages assuring a consistent split ratio across the needle valves.

The split-out portion of the primary flow passed from the switching valve and was combined with the secondary carrier flow which entered the constant temperature oven through a mass-flow sensor/controller (Brooks Model 4841, 0 to 2,000 mL/min). As in the case of the primary flow, most of the secondary flow passed through the oven and was expelled to the vent (V2) through a needle valve. A small portion (usually 10 mL/min) of the secondary flow was removed through a dual-control needle valve and passed into a switching valve (SV2). This valve functioned in an identical manner to SV1 and placed a second mass-flow sensor (Brooks, Model 5810, 0 to 100 mL/min) in the path for measuring the second split.

The split-out portion of the secondary flow passed from the switching valve and was combined with the final (tertiary) dilution stream which entered the constant temperature oven through a mass-flow sensor/controller (Brooks Model 5841, 0 to 50 L/min). This final concentration was available for sampling through a five-port manifold system that would accommodate sorbent sampling tubes. Sampling rates through the sorbent tubes were maintained by rotameters (Brooks Model 1110) at the tube exits. The unused portion of the final dilution stage was expelled to the vent (V3).

The sample generation system was connected through an eight-port (Valco) selection valve and stainless-steel tubing (1.6 mm) to a flame ionization detector. This arrangement permitted the selective monitoring of concentration levels in each of the three dilution stages and the additional monitoring of effluent from five sampling locations.

Evaluation studies have demonstrated linear concentration responses over the operational ranges of the syringe drive rate, the two split monitors, and the three dilution stages. By the appropriate selection of syringe size, drive rate, split ratios, and dilution rates, it is possible to achieve continuously variable concentrations from percent to low part-per-trillion levels using this system.

EXPERIMENTAL TEST FACILITIES

Laboratory Test Exposure Chamber

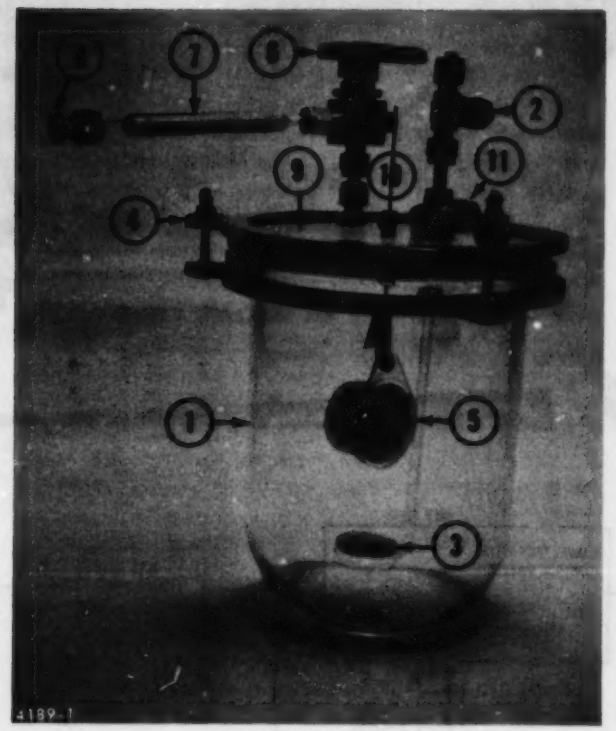
The passive sampling device were exposed to generated gas mixtures, and the concentration of the mixture was validated by a grab sample or sorbent tube (active pumped) sample. A laboratory test exposure chamber, shown in Figure 15, was used. The chamber, designed and assembled to provide test conditions for a previous dosimeter testing and evaluation program, consisted of a 2-liter borosilicate glass reaction kettle fitted with an "O"-ring-sealed Teflon lid. A standard clamp ring served to seal the lid to the glass vessel. Three ports were provided through the chamber lid. One port was used to admit test gas mixtures into the chamber. Gas line connections were made through appropriate Swagelok® fittings. The gas inlet line terminated into a coarse glass frit which promoted a more even gas flow distribution within the chamber, thus minimizing channeling effects. A second port provided an access for inserting probes into the exposure chamber for monitoring temperature and humidity within the chamber during test runs. Environmental conditions, such as temperature and humidity, could be selected and maintained over a broad range, thus providing means for evaluating dosimeter performance with respect to given environmental parameters.

The third port of the system was fitted with a three-way ball valve which could direct the gas effluent from the exposure chamber to either a vent or sample position. Sorbent tubes were used to collect known volumes of sample in order to validate gas constituent concentration(s) within the chamber during the test. Dosimeters under test were suspended above the glass frit during the exposure period. The distance between the dosimeter and gas entrance could be selected and maintained constant.

Environmental Test Chamber

Another means of exposing dosimeters to standard gas concentrations was based on the use of an environmental test chamber designed and fabricated at MRC for an ambient air passive dosimeter development program. This facility provided the means by which dosimeters could be subjected to a range of temperatures, humidities, and flow velocities, all of which could be controlled and measured. The test chamber is shown in Figure 16.

The test chamber was fabricated from thick-walled, flanged borosilicate glass pipe. In this design, a concentric tube arrangement was used. The gas was made to flow down the center tube, back through the space separating the two tubes, then down the center tube again. A variable-speed fan was used to circulate the air, and the flow velocity was controlled by adjusting the fan



(1) Pyrex exposure chamber
(2) Gas inlet fitting
(3) Glass frit
(4) Clamp ring
(5) Dosimeter under test
(6) Vent - sample selection valve
(7) Sorbent sample tube
(8) Probe inlet
(9) Teflon lid
(10) Dosimeter hanger
(11) Connection to sample pump

Figure 15. Exposure chamber for dosimeter testing and evaluation.

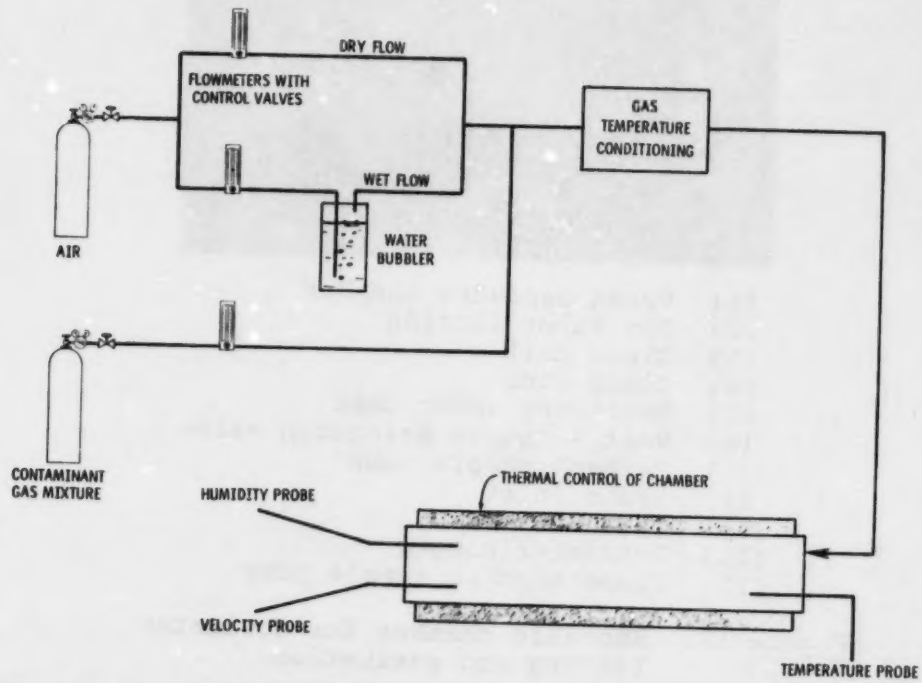


Figure 16. Environmental test chambers for exposure of monitors to selected gases and vapors.

speed. The unit could be operated under stagnant conditions, or could provide high flow regimes. The flanged ends of the chamber were provided with appropriate fittings to admit gases as well as measuring and sampling probes into the system. Gas flows were regulated, measured, and conditioned prior to entry into the chamber. The entire chamber could be heated or cooled. Humidity, likewise, could be controlled and continuously monitored. The system was completely instrumented to monitor environmental conditions within the chamber at all times.

SECTION 5

RESULTS

SORBENT SELECTION

Previous success at MRC with Porapak® R in a passive sampling device for parts-per-million sampling prompted the selection of this sorbent for initial testing in this program. Porapak R has acceptably high breakthrough volumes for the compounds of interest and good absorption/recovery efficiencies, and it provides a reasonably clean background on thermal desorption.

Porapak R sorbent was subjected to a preliminary evaluation. Compound concentrations of the order of 5 ppm were used in this phase of the study to allow solvent extraction of the dosimeters. This permitted large numbers of samples to be processed for statistical studies, and it also provided a basis for extrapolating solvent extraction data to possible detection levels with thermal desorption.

Sorbent evaluation in this work followed two routes: (1) recovery studies involving the spiking of dosimeters with the test solution, followed by solvent extraction and analysis, and (2) exposure of the dosimeters to the test compounds in the gas phase followed by solvent extraction and analysis.

Recovery results are tabulated in Table 3. Good recoveries were achieved in all instances with the lowest being approximately 83%.

A gas mixture of the 10-component spiking solution was generated by the MRC gaseous sample generating system and passed into the laboratory test exposure chamber to evaluate the performance of the passive dosimeters with the gas mixture.

The concentrations of the gas mixture components used in these exposure studies are given in Table 4. Replicates were exposed in the chamber for one- and two-hour intervals, removed, solvent extracted, and analyzed. Experimental results are included for comparison in Table 4. A statistical summary of the results in terms of retention times and responses is shown in Tables 5 and 6.

Porapak R showed promise as a candidate sorbent for this program, based on the studies involving relatively high concentrations and

TABLE 3. RECOVERY STUDIES. SPIKED DOSIMETER PACKED WITH PORAPAK R SORBENT

Compound	Spike nanograms	Nanograms recovered	Percent recovery
Methylene chloride	12	12.2	102
1,1-Dichloroethylene	12	11.2	92
1,1-Dichloroethane	12	12.6	105
Chloroform	12	12.2	102
Carbon tetrachloride	12	13.2	110
1,2-Dichloropropane	12	11.9	99
Trichloroethylene	12	11.6	97
1,1,2-Trichloroethane	12	12.0	100
Tetrachloroethylene	12	10.4	87
Chlorobenzene	12	10.0	83

TABLE 4. EXPOSURE RESULTS: DOSIMETERS LOADED WITH PORAPAK® R

Compound	Stage 1 concentration, ppm	Nanograms[a] per 5 mL MeOH extract					
		~1-hour exposure			~2-hour exposure		
		A37	A60	A81	A-17	A-33	A-34
Chloroform	7.7	1.1	1.3	1.3	2.8	3.1	2.3
		1.1	1.2	1.2	2.8	3.0	2.4
1,2-Dichloroethane	9.4	1.3	1.3	1.4	3.0	3.4	2.6
		1.1	1.3	1.5	3.1	3.2	2.7
1,1,1-Trichloroethane	7.0	1.1	1.1	1.1	2.6	3.0	2.3
		0.9	1.1	1.1	2.8	2.8	2.4
Carbon tetrachloride	6.0	1.2	1.3	1.3	2.8	3.2	2.9
		1.1	1.1	1.2	3.0	3.0	2.6
Bromodichloromethane	5.7	1.2	1.1	1.2	2.9	3.2	2.1
		0.8	0.8	1.1	3.1	3.1	2.4
Trichloroethylene	7.0	1.1	1.1	1.3	3.0	3.3	2.7
		1.0	1.1	1.3	3.1	3.1	2.5
1,1,2-Trichloroethane	7.0	1.3	1.2	1.3	3.2	3.4	2.8
		1.1	1.2	1.3	3.3	3.2	2.8
		1.0					
Tetrachloroethylene	5.7	1.8	1.9	1.7	3.6	3.7	3.1
		1.6	1.8	2.3	3.4	3.4	3.2
Chlorobenzene	8.2	1.6	1.4	1.0	4.4	3.1	4.0
		1.2	1.6	2.0	2.6	2.9	2.4

[a]Based on relative response to a 10-ng standard mixture 1920050-2.

TABLE 5. STATISTICAL SUMMARY OF 1-HOUR EXPOSURE TESTS

Mean	Standard deviation	Relative standard deviation, %	Number of times found	Peak name
Retention time				
4.39	0.002	0.04	3	Methylene chloride
6.19	0.003	0.04	3	1,1-Dichloroethylene
7.28	0.006	0.08	3	1,1-Dichloroethane
8.34	0.000	0.00	3	Chloroform
10.59	0.000	0.00	3	Carbon tetrachloride
12.44	0.000	0.00	3	1,2-Dichloropropane
13.17	0.000	0.00	3	Trichloroethylene
13.96	0.008	0.06	3	1,1,2-Trichloroethane
19.04	0.000	0.00	3	Tetrachloroethylene
21.83	0.000	0.00	3	Chlorobenzene
Print areas				
117279	1968	1.7	3	Methylene chloride
73488	2220	3.0	3	1,1-Dichloroethylene
104621	4407	4.2	3	1,1-Dichloroethane
176548	3356	1.9	3	Chloroform
121947	4013	3.3	3	Carbon tetrachloride
92004	1243	1.4	3	1,2-Dichloropropane
135142	4339	3.2	3	Trichloroethylene
259195	7458	2.9	3	1,1,2-Trichloroethane
173555	10513	6.1	3	Tetrachloroethylene
69584	8657	12.4	3	Chlorobenzene

solvent extraction procedures. Laboratory studies indicated that high sample recoveries were achieved in direct sample spiking experiments as well as with gas sample exposures.

A linear concentration-time relationship could be reasonably predicted from the one- and two-hour exposure studies. Data gained under these exposure conditions showed good replication. Extrapolation of data gained at the sample concentration level/sample desorption mode employed for this program phase would indicate that the device loaded with Porapak R should be sensitive in the low-ppb range if the device were properly scaled-up and thermal desorption was employed.

In order to verify predicted performance, measurements were made at the 1-ppb concentration level using thermal desorption instead of solvent extraction procedures. During this study, passive dosimeters were exposed to the 10-component gas mixtures generated

TABLE 6. STATISTICAL SUMMARY OF 2-HOUR EXPOSURE TESTS

Mean	Standard deviation	Relative standard deviation, %	Number of times found	Peak name
Retention time				
4.40	0.000	0.00	3	Methylene chloride
6.21	0.000	0.00	3	1,1-Dichloroethylene
7.29	0.000	0.00	3	1,1-Dichloroethane
8.26	0.000	0.00	3	Chloroform
10.61	0.000	0.00	3	Carbon tetrachloride
12.45	0.000	0.00	3	1,2-Dichloropropane
13.17	0.000	0.00	3	Trichloroethylene
13.97	0.008	0.06	3	1,1,2-Trichloroethane
19.04	0.011	0.06	3	Tetrachloroethylene
21.83	0.000	0.00	3	Chlorobenzene
Print areas				
55255	4431	8.0	3	Methylene chloride
19627	3832	19.5	3	1,1-Dichloroethylene
44317	5017	11.3	3	1,1-Dichloroethane
77109	6451	8.4	3	Chloroform
48090	5396	11.2	3	Carbon tetrachloride
38363	1809	4.7	3	1,2-Dichloropropane
62704	4255	6.8	3	Trichloroethylene
110512	4417	4.0	3	1,1,2-Trichloroethane
79673	2502	3.1	3	Tetrachloroethylene
31446	6749	21.5	3	Chlorobenzene

in the sample generation system. The concentration of each component was maintained at approximately 1 ppb, and exposure times varied from 1 to 3 hours. The exposure procedure and facility used in this study was that described earlier. After exposure, the dosimeter were thermally desorbed and analyzed. Results are shown in Table 7.

Results gained with Porapak R elements at the 1-ppb level demonstrated the capability of monitoring at this level under ambient air conditions. Unfortunately, recovery efficiencies at the low concentration levels were considerably lower (40% to 50%) than those achieved with spiked samples. Recovery of chlorobenzene was particularly poor and in many cases uncertain. The performance of the Porapak R elements seemed to decrease with increased use; this was due primarily to the high desorption temperature (~190°C) required, which undoubtedly led to sorbent degradation.

TABLE 7. THERMAL DESORPTION OF PASSIVE DOSIMETER PACKED WITH PORAPAK R: EXPOSURE STUDIES AT THE 1-ppbv LEVEL

Sample exposure hour	Concentration, nanograms						
	Chloro-form	1,2-Dichloro-ethane	Carbon tetra-chloride	Trichloro-ethylene	1,1,2-Trichloro-ethane	Tetra-chloro-ethylene	Chloro-benzene
1	6.6	4.7	10	7.0	2.4	4.2	2.5
2	8.6	8.7	13	12	4.5	6.6	-
3	17	18	22	22	14	16	3.0

In an effort to improve performance, dosimeters were prepared using Tenax GC porous polymer. Exposure studies with these elements were much more encouraging with recovery efficiencies for all components greater than 93%. One-hour exposures to the seven-component test gas at the 1-ppb level gave excellent results and indicated that Tenax was the better choice of sorbent.

DOSIMETER PERFORMANCE TESTING

Dosimeter Response to Compounds of Interest

A comprehensive laboratory study was conducted to establish dosimeter response to varying concentrations of the compounds of interest. Tenax GC was employed as the sorbent in all cases. Initially, dosimeters were spiked by liquid injection of standard into the dosimeters, thermally desorbed, and analyzed. Results of these measurements are plotted in Figures 17 and 18. A linear response was obtained for each compound over the concentration range covered. This range should adequately cover compound concentrations encountered in ambient air monitoring. In addition to liquid spiking of the dosimeters, gas spiking was accomplished by exposing the dosimeters to gas standards generated by the sample generation system. Compounds generated and the concentration of the compound at the three dilution stages are presented in Table 8. Results were similar to those obtained with liquid spikes. One-hour dosimeter exposures to Stage 3 of the sample generation system gave recoveries of approximately 30 ng for each compound. The gas components concentration at Stage 3 is on the order of 1-ppbv, thereby indicating dosimeter sensitivity considerably below the 1-ppbv level. Gas chromatographic detection sensitivity of approximately 1 ng was obtained with this system.

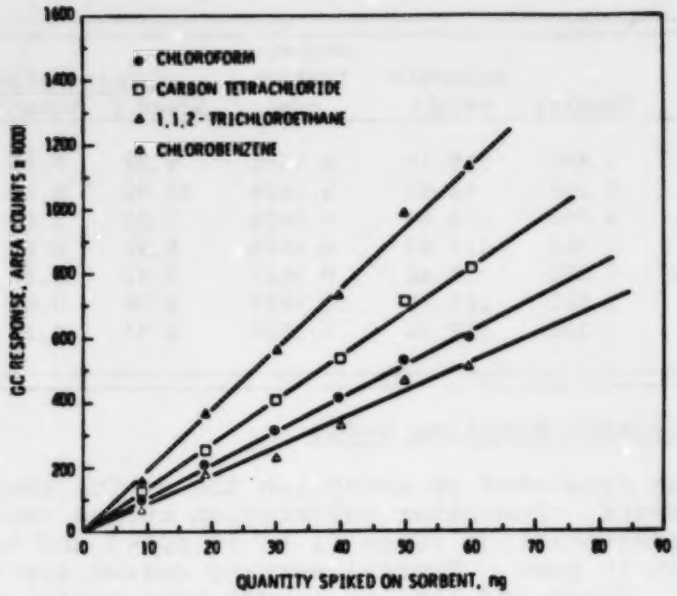


Figure 17. Recovery of chemicals from dosimeter by thermal desorption.

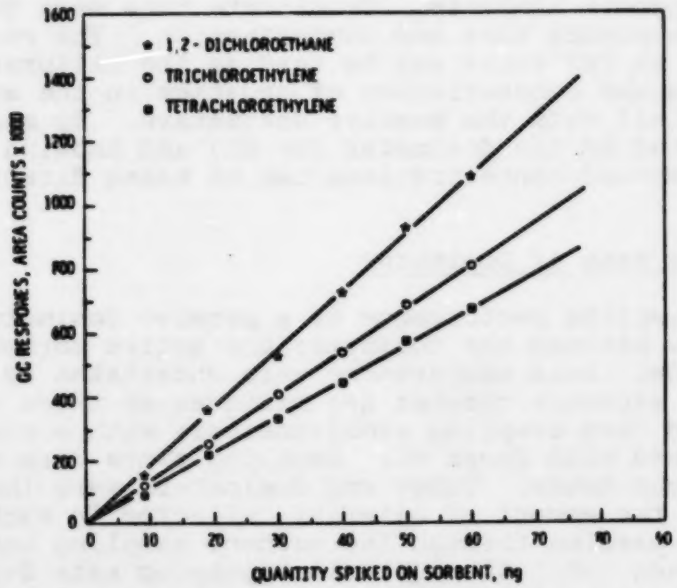


Figure 18. Recovery of chemicals from dosimeter by thermal desorption.

TABLE 8. SAMPLE GENERATION SYSTEM SUMMARY

Compound	Density	Molecular weight	Concentration, g/mL	Concentration, ppm Stage 1	Stage 2	Stage 3
Chloroform	1.492	119.39	0.1625	9.39	0.12	0.0012
1,2-Dichloroethane	1.256	98.97	0.1624	11.32	0.14	0.0014
Carbon tetrachloride	1.592	153.84	0.1624	7.28	0.09	0.0009
Trichloroethylene	1.462	131.40	0.1625	8.52	0.11	0.0010
1,1,2-Trichloroethane	1.435	133.42	0.1627	8.41	0.10	0.0010
Tetrachloroethylene	1.623	165.85	0.1625	6.76	0.08	0.0008
Chlorobenzene	1.106	112.56	0.1628	9.97	0.12	0.0012

Determination of Dynamic Sampling Range

Laboratory work was conducted to establish the useful sampling range of the dosimeter. Dosimeter calibration curves were developed for the low concentration range (1 to 50 ppbv) and extended up to approximately 10 ppmv. Typical working curves are shown in Figures 19 and 20. These and similar curves were established by exposing dosimeters in the sample exposure chamber for varying times and concentrations. Sample concentrations in the exposure chamber were validated by passing a known sample volume through an actively pumped solid Tenax sampling tube, thermal desorption, and gas chromatographic analysis. Triplicate runs were generally made for a given exposure time and concentration. The resulting dosimeter loading vs CxT curve may be used as the calibration curve to determine the concentration of organics in the air when sampling in the field with the passive dosimeters. By measuring the amount collected by the dosimeter (by GC) and knowing the exposure time, compound concentrations can be taken directly from the curve.

Equivalent Pumping Rate of Dosimeter

To evaluate the sampling performance of a passive dosimeter system, direct comparisons between the dosimeter and active sorbent sampling tubes were made. Such comparisons were undertaken by exposing dosimeters in the exposure chamber gas mixtures at these concentration levels and then sampling simultaneously with a sorbent sampling tube packed with Tenax GC. Sampling times were varied between one and four hours. Tubes and dosimeters were then analyzed to determine the amount of material collected in each case. The volume of air passing through the sorbent sampling tube was measured during each run. The equivalent pumping rate for the passive dosimeter was calculated (the mass of material collected by the dosimeter was divided by the mass/volume ratio given by the sorbent sampling tube). Initial determinations were made employing the dosimeter in a dual face sampling mode. An equivalent

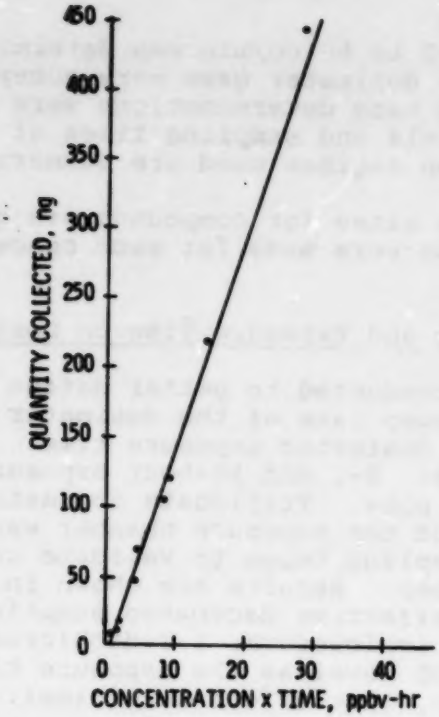


Figure 19. Response curve (chlorobenzene).

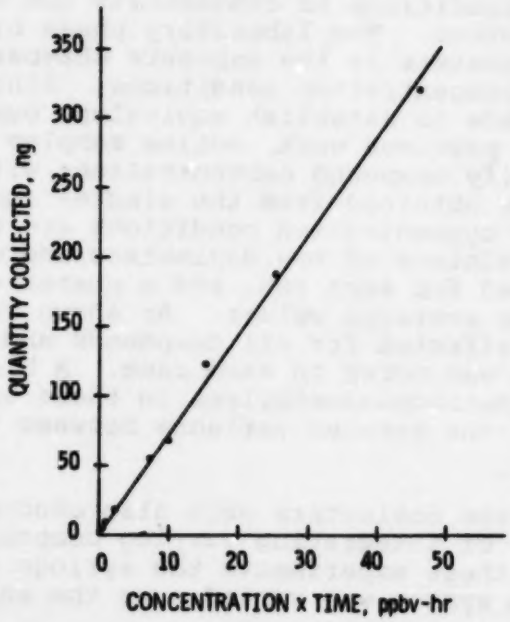


Figure 20. Response curve (1,2-dichloroethane).

sample pumping rate of 50 to 60 cc/min was determined. Used in the single-face mode the dosimeter gave more acceptable sampling performance, and pumping rate determinations were made at three sample concentration levels and sampling times of 1, 2, and 4 hours. The concentration regimes used are summarized in Table 9.

Averaged equivalent pump rates for compounds are given in Table 10. Triplicate determinations were made for each concentration and sampling time.

Effects of Concentration and Exposure Time on Dosimeter Pump Rate

A laboratory study was conducted to better define the relationship between the equivalent pump rate of the dosimeter and sampled compound concentration and dosimeter exposure time. Pump rates were determined for 1-, 2-, 4-, 8-, and 16-hour exposures at concentrations of 1, 10, and 100 ppbv. Triplicate dosimeters were exposed under each condition, and the exposure chamber was sampled during each run with active sampling tubes to validate compound concentration within the chamber. Results are shown in Figure 21. The general trend shows an effective decreased sampling rate for the most volatile compounds (chloroform, 1,2-dichloroethane, and carbon tetrachloride) at the ppb level as the exposure time is increased. At higher concentrations, this effect is minimal.

Dosimeter Sampling Tests

A number of validation tests were conducted in the laboratory and under field sampling conditions to demonstrate the sampling performance of the dosimeters. The laboratory phase of this study involved exposing dosimeters in the exposure chamber under both constant and varying concentration conditions. Single- and dual-face exposures were made to establish equivalent pump rate relationships. As in previous work, active samples were taken simultaneously to verify compound concentrations within the exposure chamber. Results obtained from the single- and dual-face exposures to constant concentration conditions are given in Tables 11 and 12. A minimum of two dosimeters and one active sampling tube were used for each run, and a number of replicates were made to determine averaged values. As shown in the tables, good recoveries were effected for all compounds and good tube/dosimeter correlation was noted in each case. A high blank reading was observed for tetrachloroethylene in these trials which probably accounts for the greater variance between tube and dosimeter analyses.

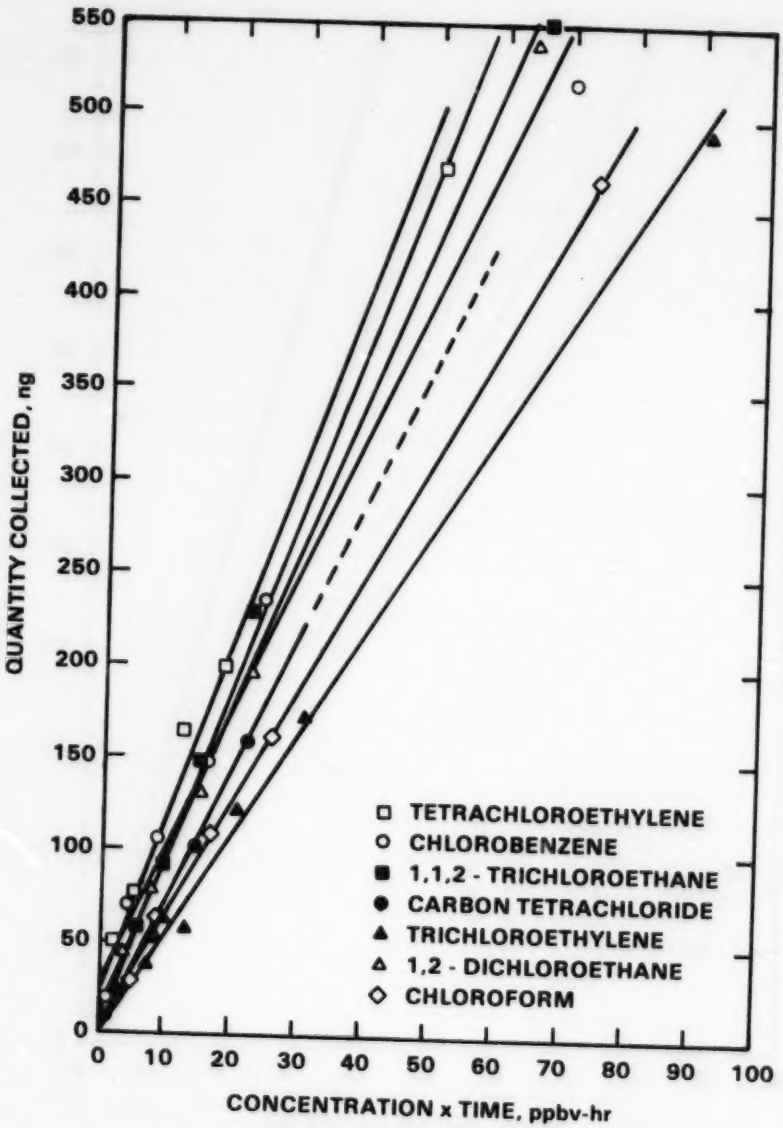
Chamber exposures of the dosimeters were also conducted to demonstrate the capability of integrating varying compound concentrations over time. In these experiments the syringe drive rate on the sample generation system was varied over the exposure time in

TABLE 9. EXPOSURE CONCENTRATIONS FOR PUMP RATE DETERMINATION (ppbv)

Sample generation parameters	Chloroform	1,2-Dichloroethane	Carbon tetrachloride	Trichloroethylene	1,1,2-Trichloroethane	Tetrachloroethylene	Chlorobenzene
Stage 3, 25% of $\frac{1}{1000}$ range	0.71	0.83	0.44	0.54	0.50	0.47	0.54
Stage 3, 25% of $\frac{1}{100}$ range	8.21	10.04	7.20	7.56	7.92	5.99	8.15
Stage 2, 25% of $\frac{1}{1000}$ range	71.97	78.16	73.81	65.49	64.61	49.81	69.34

TABLE 10. AVERAGE EQUIVALENT PUMP RATES (SINGLE-FACED SAMPLING)

	Chloroform	1,2-Dichloroethane	Carbon tetrachloride	Trichloroethylene	1,1,2-Trichloroethane	Tetrachloroethylene	Chlorobenzene
Pump rate, cc/min	25.0	26.8	21.8	28.3	27.7	29.5	34.3
Std. dev.	±5.0	±2.9	±5.2	±1.5	±0.6	±1.9	±4.0



(continued)

Figure 21. Dosimeter response--sampling time--compound volatility relationship.

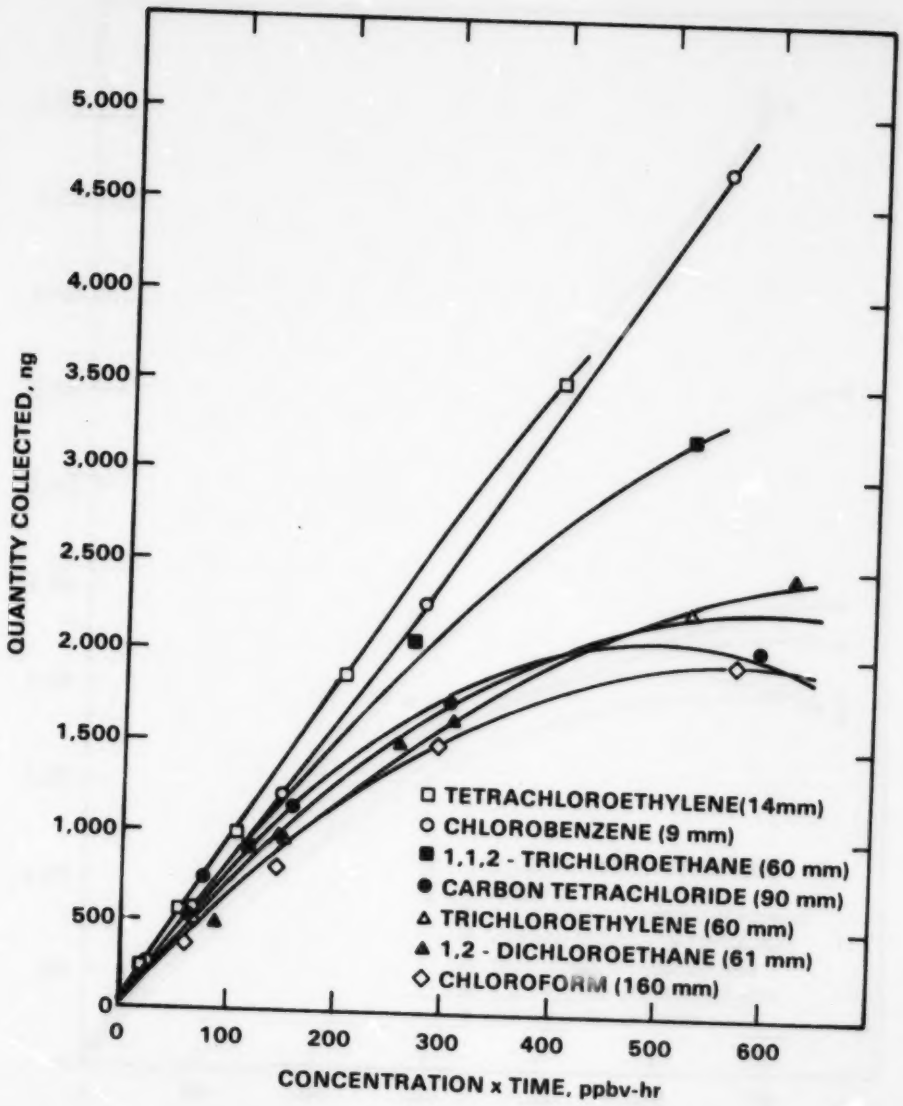


Figure 21 (continued)

TABLE 11. DUAL-FACE SAMPLING FOR 45 MINUTES

Compound	Concentration, ppb		Percent recovery	Concentration, ppbv	Ratio dosimeter/ tube
	Theory	Tube		Dosimeter	
Chloroform	11.6	11.5	100	8.7	0.76
1,2-Dichloroethane	13.9	14.0	100	9.1	0.65
Carbon tetrachloride	9.0	11.7	130	8.9	0.76
Trichloroethylene	10.5	9.8	93	9.6	0.98
1,1,2-Trichloroethane	10.3	10.6	103	10.3	0.97
Tetrachloroethylene	8.3	8.5	102	10.6	1.25
Chlorobenzene	12.3	9.5	77	11.2	1.18

TABLE 12. SINGLE-FACE SAMPLING FOR ONE HOUR

Compound	Concentration, ppb		Percent recovery	Concentration, ppbv	Ratio dosimeter/ tube
	Theory	Tube		Dosimeter	
Chloroform	11.6	11.1	96	12.9	1.17
1,2-Dichloroethane	13.7	13.7	100	13.8	1.00
Carbon tetrachloride	8.8	10.6	120	9.7	0.91
Trichloroethylene	10.4	10.2	98	12.1	1.19
1,1,2-Trichloroethane	10.2	11.1	109	12.5	1.13
Tetrachloroethylene	8.2	8.6	105	13.7	1.59
Chlorobenzene	12.1	11.0	91	12.4	1.13

order to vary the exposure concentration. An active tube was used to sample the exposure chamber during the exposure to verify compound concentrations. Concentrations were varied from 1 ppbv to 10 ppbv to 100 ppbv. Results of these experiments are shown in Tables 13 and 14. Performance was equivalent to that demonstrated at constant concentration conditions.

TABLE 13. DUAL-FACE SAMPLING INTEGRATION EXPERIMENT A
(1 ppbv - 40 min; 10 ppbv - 10 min; 100 ppbv - 10 min)

Compound	Concentration, ppbv		Percent recovery	Concentration, ppbv	Ratio dosimeter/ tube
	Theory	Tube		Dosimeter	
Chloroform	22.0	22.7	103	23.9	1.05
1,2-Dichloroethane	26.6	26.6	100	24.7	0.93
Carbon tetrachloride	17.0	21.3	125	20.5	0.96
Trichloroethylene	20.0	20.9	105	25.0	1.20
1,1,2-Trichloroethane	19.7	21.5	109	24.7	1.15
Tetrachloroethylene	15.8	16.6	105	24.5	1.48
Chlorobenzene	23.4	24.4	104	25.3	1.04

TABLE 14. DUAL-FACE SAMPLING INTEGRATION EXPERIMENT B
(1 ppbv - 45 min; 100 ppbv - 15 min)

Compound	Concentration, ppbv		Percent recovery	Concentration, ppbv	Ratio dosimeter/ tube
	Theory	Tube		Dosimeter	
Chloroform	28.0	26.5	95	26.7	1.01
1,2-Dichloroethane	33.8	33.6	99	28.1	0.84
Carbon tetrachloride	21.7	22.6	104	24.0	1.06
Trichloroethylene	25.4	24.3	96	27.7	1.14
1,1,2-Trichloroethane	25.0	26.7	107	29.8	1.12
Tetrachloroethylene	20.1	19.8	99	28.8	1.43
Chlorobenzene	29.7	32.0	108	33.9	1.06

Storage Test

A cursory study was carried out to determine the extent to which compounds were lost during storage. Initial storage tests involved exposing a series of dosimeters to the test gas mixture at the 1-ppb level and following compound recovery with respect to time.

The dosimeters were loaded with approximately 30 ng of each compound. Replicate dosimeters were analyzed initially to establish the concentration based at the beginning of storage. The remainder of the dosimeters were capped with friction-tight Teflon caps*, sealed in screw-cap glass jars, and maintained under ambient laboratory conditions for twelve days. Results of this study are given in Table 15.

*Later studies used polyethylene caps.

TABLE 15. STORAGE TEST RESULTS

Compound	At beginning of storage, ng	After 12 days, ng	Percent change
Chloroform	25.0	22.4	10
1,2-Dichloroethane	23.3	21.0	10
Carbon tetrachloride	21.0	10.5	50
Trichloroethylene	24.3	20.0	18
1,1,2-Trichloroethane	27.5	23.2	16
Tetrachloroethylene	29.7	26.6	10
Chlorobenzene	32.1	27.0	15

As indicated by the results in the Table 15, anomolous behavior was observed in the case of carbon tetrachloride, showing a decrease of 50% over the 12-day period. Recoveries of other compounds were at an acceptable level but may be improved by a better packaging concept or by some environmental control depending on the underlying reasons (e.g., irreversible adsorption).

Effects of Air Velocity and Humidity

The effect of air flow velocity on dosimeter performance has been studied under laboratory and field conditions. The dosimeter is designed to minimize face velocity effects. In the laboratory, sample flow rates through the exposure chamber of 300 cc/min and 3.5 L/min gave equivalent sample collection efficiency. Under field sampling conditions, dosimeters oriented with the wind normal to the face and at right angles to the wind direction gave similar results (see Table 17). Wind velocities up to 20 mph were observed during this study. Humidity and temperature effects were of little or no consequence as indicated by our on-site "field" studies (see On-Site Air Sampling section). Temperature and humidity readings around 90°F and 80% relative humidity were observed during the test period, and dosimeter performance remained at a very acceptable level.

Dosimeter Conditioning and Packaging Procedure

Successful application of the passive dosimeter to real monitoring problems hinges not only on the "analytical properties" of the device, but also on achieving and maintaining a clean background prior to sampling as well as after sampling has been completed.

Precautions that should be taken to prevent contamination of the sorbent cartridge during its preparation include handling all materials while wearing protective gloves and/or using clean utensils; using high-purity, distilled-in-glass solvents; using Teflon tape or Teflon sleeves instead of silicone grease at

Soxhlet extractor glass joints; placing a charcoal trap in the vacuum line of a vacuum oven system to prevent the contamination of drying materials by the back-diffusion of pump lubricants; and many others (which have been previously stated). The purpose of cleaning the sorbent and other materials, taking precautions to prevent contamination during sorbent cartridge preparation, and conditioning the sorbent cartridges within approximately one week of sample collection is to assure that the sorbent cartridges have minimal levels of background and contamination.

Although contamination can contribute to the background (materials present during a sorbent cartridge analysis when no materials have been added to the cartridge [i.e., a blank]) present on a sorbent cartridge, the sorbent material itself can contribute background through slow degradation (or "aging"). For this reason, a sorbent cartridge should be reconditioned just prior to sampling if it has been stored for more than approximately one week. However, the thermal or chemical decomposition of a sorbent caused by sampling/analytical conditions also can significantly contribute to sorbent cartridge backgrounds. Thermal decomposition of a sorbent results, from overheating the sorbent cartridge during conditioning, sampling, or desorption. Hence, sorbent cartridges should not be exposed to temperatures above their temperature limits. Chemical decomposition caused by exposing the sorbent cartridges to inappropriate solvents also should be avoided. Chemical decomposition also may be caused by reactive species (such as NO_x, SO_2, and HCl) in the sample matrix which, if anticipated, can be potentially removed by selective filters placed prior to the sorbent cartridge; however, reactive species should not present a major problem with ambient air samples.

Usually, the analyses of "blank" sorbent cartridges is enough to indicate the type of compounds and their levels that comprise the sorbent background. Quite often, the background (of a particular sorbent) from many "blank" tubes may vary somewhat in amount, as indicated by peak sizes (or areas), but it may retain a certain pattern (i.e., peaks from various analyses have similar retention times and similar chemical type). This pattern is probably due to compounds produced by sorbent decomposition which is typical for that particular sorbent because of the chemical composition of the sorbent.

Knowing the types of decomposition products to expect from a particular sorbent, one can determine whether thermal or chemical decomposition of the sorbent occurred during sample collection, such as from matrix effects. Therefore, one can evaluate whether the compounds detected during an analysis of a sorbent cartridge sample are the result of the collected sample or some type of sorbent decomposition.

Sorbent background levels are reduced to a minimum through cleaning and conditioning. This minimal background level is maintained by storing the tubes capped with metal fittings and O-rings inside a culture tube with a Teflon-lined screw-top cap. The hardware needed for the storage of each sorbent tube is described in Table 16 and the use of these materials for tube storage is demonstrated by Figure 22.

TABLE 16. HARDWARE MATERIALS REQUIRED FOR STORAGE OF EACH SORBENT TUBE

Item	Material	Size-brand	Quantity
Nut	Stainless steel	6.4 mm (1/4 in.)-Swagelok	Two
Front ferrule	Stainless steel	6.4 mm (1/4 in.)-Swagelok	Two
Cap	Stainless steel	6.4 mm (1/4 in.)-Swagelok	Two
O-ring	Viton	~6.4 mm (~1/4 in.)-O.D.	Two
Culture tube	Glass	20 cm long x 2.5 cm diameter-Pyrex, Kimax or equivalent	One
Culture tube screw-top cap	Plastic, with Teflon liner	For 2.5 cm diameter culture tube	One

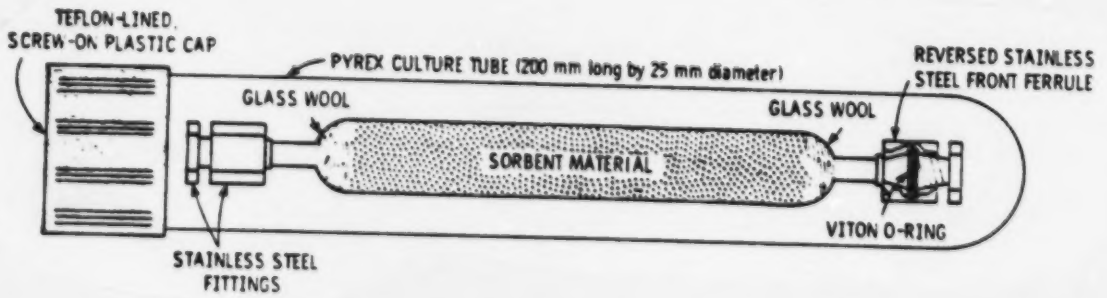


Figure 22. Storage of a sorbent tube.

Dosimeter cleanup is accomplished by Soxhlet extraction and thermal desorption. Approximately twenty dosimeters can be desorbed simultaneously with the facilities in place at MRC. This capacity, however, could easily be increased should the need arise. Dosimeters are stacked face-to-face in a stainless steel thin-wall

tube closed off at one end and fitted with a 1/4-in. Swagelock fitting. A gas line attached to the end of the tube allows a stream of nitrogen to be passed through the dosimeter stack during desorption. The containment tube and dosimeters are placed in an oven maintained at 250°C. Dosimeters are desorbed for 24 hours. Once desorbed, the dosimeters are placed in preheated borosiliate glass jars while hot, capped-off, and transferred to a nitrogen-purged glove box for packaging.

A dosimeter storage package was designed to ensure transport of clean dosimeters to the test site and to maintain sample integrity during shipment back to the laboratory for analysis. The packaging steps are shown in Figure 23. In Step 1, a friction tight linear polyethylene cap (Caplug #EC-24) is placed over the dosimeter leaving one face exposed. This is the configuration of the dosimeter for single-face sampling. A second cap (Caplug #WW-18), shown in Step 2, covers the exposed dosimeter face during storage and transport, forming a tight seal when pressed down fully on the initially capped dosimeter in Step 1. This seal is shown clearly in Step 3. The over cap is removed at the time sampling is to begin.

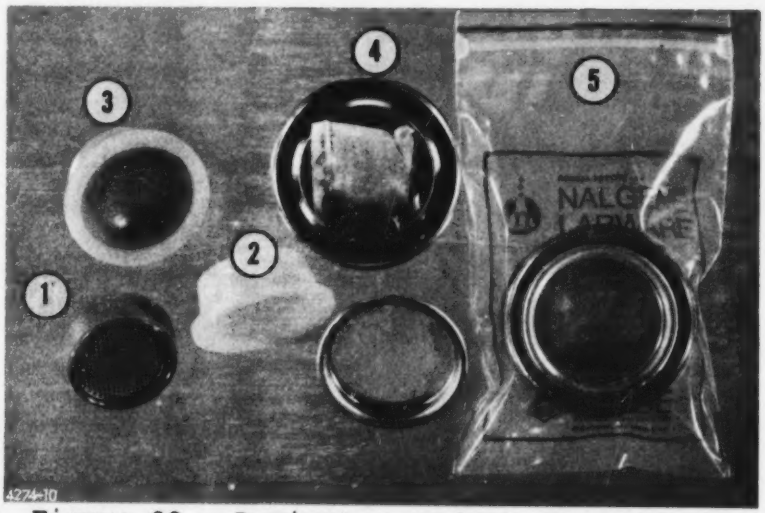


Figure 23. Dosimeter package elements.

Once fully capped, the dosimeter is sealed in a friction lid metal can (Step 4). These cans are pretreated by baking in an oven at 250°C for 2 to 4 hours to remove volatile from the metal surfaces. The can is then closed and placed (Step 5) in a double lock polyethylene bag. Activated charcoal is placed in the bag with the capped dosimeter to preferentially trap organic contaminants during storage and transit.

SECTION 6

SAMPLING PERFORMANCE

ON-SITE AMBIENT AIR SAMPLING STUDIES

In order to assess dosimeter performance under actual ambient air monitoring conditions, several dosimeters were exposed around the laboratory perimeter between June 30 and November 4, 1981 to determine if any chlorinated compounds could be detected in this area. Various industries surround the site, spiked dosimeters were exposed as controls, and laboratory dosimeter blanks were run to determine if any contamination was experienced in handling and analyzing the dosimeters in the laboratory. Chromatograms obtained from dosimeters exposed on the various days are shown in Figure 24. Tabulated data from these tests are given in Table 17. All exposures were for two hours. Ambient conditions varied somewhat from day to day. Fahrenheit temperatures during this period ranged from high 80's to low 90's, and relative humidities ranged from 50 to 80%. Wind velocities ranged from approximately 5 to 25 mph.

As is shown in Table 17, good recoveries of the laboratory spikes were achieved. Carbon tetrachloride, trichloroethylene, tetrachloroethylene, and chlorobenzene were found in the air. Laboratory dosimeter blanks gave no indication of significant backgrounds of these compounds. Chromatograms obtained for the different days showed interesting variation with respect to both compounds found and compound concentration. Compound identification was on the basis of retention times, which correlated exactly with those determined for the standards of the compounds. Compounds were also verified by source identification. For example, the high results obtained on July 6 originated from a dumpster upwind of the sampling site. A number of cleaning rags containing solvents were found in the dumpster. Interestingly, samples were taken on November 4 to check the level of chlorobenzene in the area. On this date, a process was put into service which utilized chlorobenzene as a solvent, and the results showed a chlorobenzene level well above anything obtained in prior samplings.

DOSIMETER FIELD TESTS

Three different field evaluation studies were conducted with the passive dosimeter during this program. One involved sampling for chlorinated organics as part of a formaldehyde study being conducted by NIOSH and EPA. In this study, the passive dosimeter was

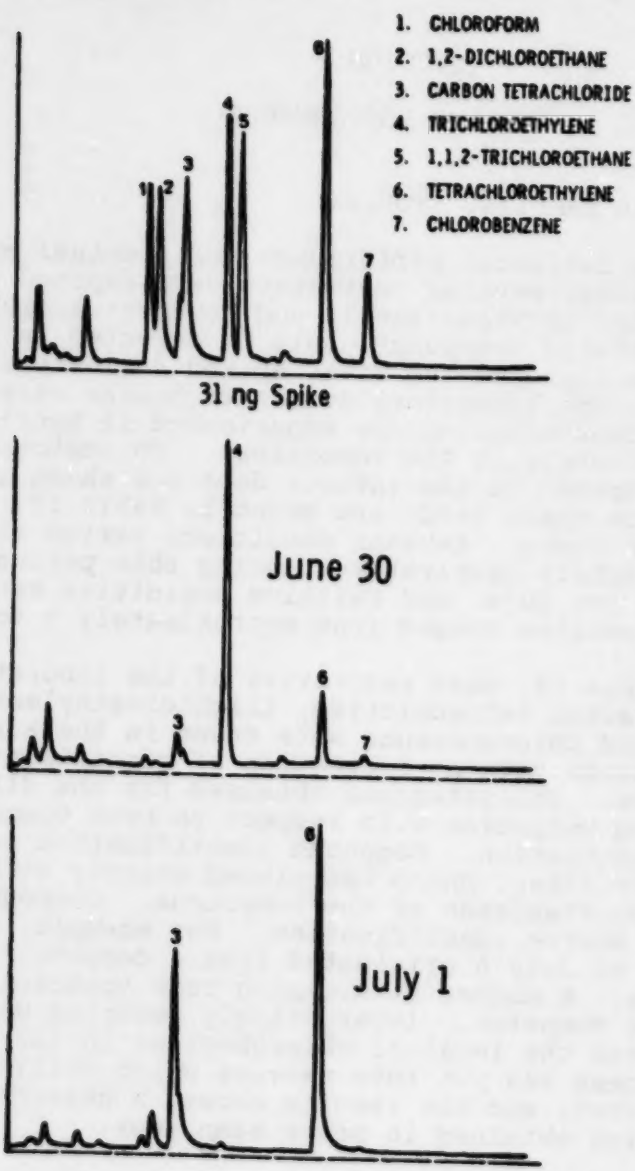


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Figure 24. Field sample chromatograms.

DOSIMETER AMBIENT AIR EXPOSURES (cont)

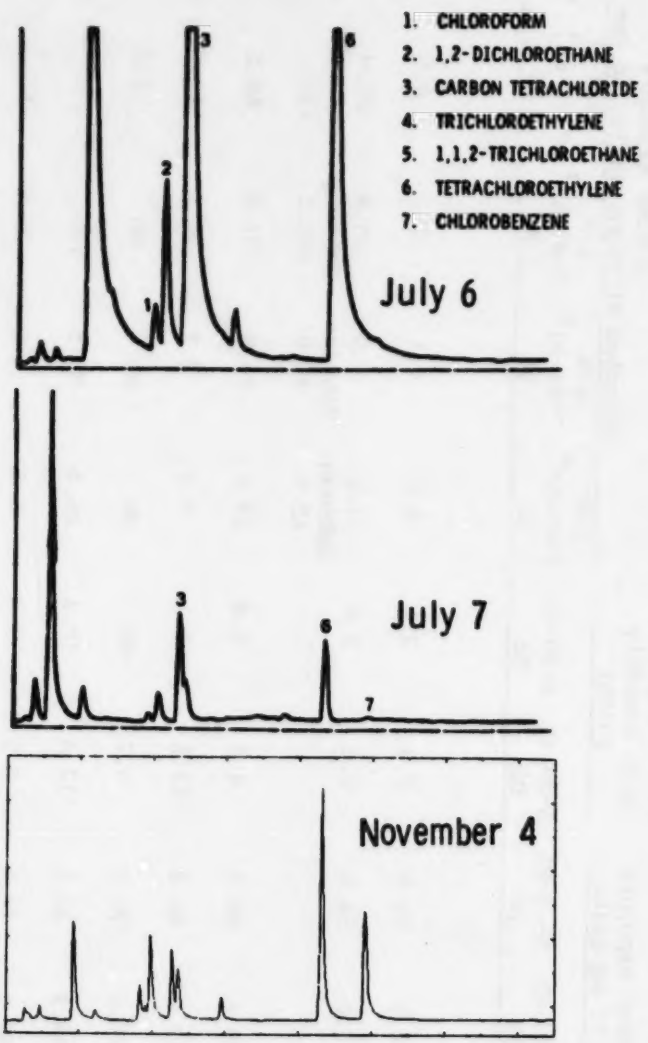


Figure 24 (continued)

TABLE 17. AMBIENT AIR EXPOSURE OF PASSIVE DOSIMETER

	2-hour exposure + 31 mg spike		2-hour exposure high humidity (~70%)		2-hour exposure oriented at right angles to one another					
Sample date:	6-29-81	6-29-81	6-30-81	6-30-81	E-W 7-01-81[a]	N-S 7-01-81[a]	E-W 7-02-81[a]	N-S 7-02-81[a]	N-S 7-06-81[a]	E-W 7-06-81[a]
Dosimeter No.:	D2	D7	D2	D5	D1	D6	D1	D5	D5	D7
Compound										
1	32.5	36.9	2.5	3.1	4.0	4.1	9.5	8.5	4.4	2.1
2	30.0	34.4	0.8	1.0	12.2	9.5	25.8	20.9	6.7	6.2
					Unknown 42.2	Unknown 33.9	Unknown 136.1	Unknown 135	Unknown 18.7	Unknown 17.0
3	39.6	16.9	4.0	8.4	25.4	20.6	73.8	68.2	16.8	11.0
4	43.2	40.8	51.2	108	3.4	2.7	18.8	12.1	4.2	2.6
5	27.4	22.2	0.7	ND	ND	ND	ND	1.0	1.8	2.0
6	44.9	51.1	12.4	10.3	86.4	93.5	175	173	12.8	12.5
7	40.1	44.6	7.2	7.3	5.5	4.2	28.6	ND	4.8	4.9

[a]Wind W to E.

employed as a personal monitor. Personal monitoring was conducted on an individual traveling to and from work, at work, and in the home environment. Another field evaluation involved a work station monitoring situation for 1,2-dichloroethane in a chemical manufacturing plant in which sampling was conducted simultaneously with charcoal tubes and the MRC passive device. An additional work station sampling which compared dosimeter results with these obtained from solid sorbent sampling tubes was included in this study. A third study involved sampling in a laboratory at the Environmental Protection Agency facility in Research Triangle Park by EPA personnel.

Results of the personal monitoring tests are given in Table 18. Chlorinated material collected in the home environment and in-transit to and from work was negligible. Interestingly, the personal exposure level measured in the work area compares favorably with other work station monitoring data (Table 19) taken concurrently with this study.

Work station monitoring results showing comparisons between dosimeters and charcoal and solid sorbent tubes, respectively, are given in Tables 19 and 20. Good agreement was achieved between the charcoal tubes and the passive device, with one exception. This was most likely due to the position of the passive dosimeter with respect to the charcoal sampling tube. The former was shielded by protective clothing, thus minimizing the overall exposure of the device.

In general, the laboratory exposures at EPA showed very low levels of chlorinated hydrocarbons. All of the samples were analyzed in blind faction. Carbon tetrachloride and trichlorofluoromethane were the only compounds found to a greater extent in some of the samples compared to the others. Because there were to be two field blanks, it was assumed that dosimeters 47 and 48 with low levels of these compounds were the field blanks.

The concentration of these compounds found using the passive dosimeters (assuming two sided sampling) was as follows:

Carbon tetrachloride	1 ppbv
Trichlorofluoromethane	18 ppbv

Trace amounts (1 ppb or less) of eight other chlorinated hydrocarbons were found in both the samples and the field blanks. In general, even lower quantities of these compounds were found in retained laboratory blanks. The variation between the background found on the lab blanks and the field blanks, even though it is at the 1 ppb level, has led us to revise our packaging methods to achieve even lower background. Reconstructed chromatograms of the dosimeters explored in this study are shown in Figures 25, 26, and 27.

TABLE 18. PASSIVE DOSIMETER PERSONAL MONITORING STUDY

	Home area, Dosimeter No. 45			Transit to work, Dosimeter No. 42			Work area, Dosimeter No. 45		
	Amount collected, ng	Exp. time, hours	Concentration, ppbv	Amount collected, ng	Exp. time, hours	Concentration, ppbv	Amount collected, ng	Exp. time, hours	Concentration, ppbv
Chloroform	3	12.9	0.006	ND	0.90	ND	2	7.85	-
1,2-Dichloroethane		12.9	-	ND	0.90	ND	-	7.85	-
Carbon tetrachloride		12.9	-	ND	0.90	ND	42	7.85	0.68
Trichloroethylene		12.9	-	ND	0.90	ND	53	7.85	0.87
1,1,2-Trichloroethane		12.9	-	ND	0.90	ND	8	7.85	0.10
Tetrachloroethylene	79	12.9	0.81	ND	0.90	ND	99	7.85	1.67
Chlorobenzene	0.9	12.9	-	ND	0.90	ND	4,100	7.85	70.8

	Transit from work, Dosimeter No. 48			Home area, Dosimeter No. 49		
	Amount collected, ng	Exp. time, hours	Concentration, ppbv	Amount collected, ng	Exp. time, hours	Concentration, ppbv
Chloroform	ND	0.58	ND	-	12.37	-
1,2-Dichloroethane	ND	0.58	ND	-	12.37	-
Carbon tetrachloride	ND	0.58	ND	-	12.37	-
Trichloroethylene	ND	0.58	ND	21	12.37	0.20
1,1,2-Trichloroethane	ND	0.58	ND	-	12.37	-
Tetrachloroethylene	ND	0.58	ND	-	12.37	-
Chlorobenzene	ND	0.58	ND	1	12.37	-

(continued)

TABLE 18 (continued)

	Home area			Work area			Work area		
	Dosimeter No. 43			Dosimeter No. 41			Dosimeter No. 44[a]		
	Amount collected, ng	Exp. time, hours	Concentration, ppbv	Amount collected, ng	Exp. time, hours	Concentration, ppbv	Amount collected, ng	Exp. time, hours	Concentration, ppbv
Chloroform		0.47			8.05		3	0.5	0.04
1,2-Dichloroethane		0.47			8.05			0.5	
Carbon tetrachloride		0.47			8.05			0.5	
Trichloroethylene		0.47		103	8.05	1.70		0.5	
1,1,2-Trichloroethane		0.47			8.05			0.5	
Tetrachloroethylene	0.7	0.47	-	12	8.05	0.16	2	0.5	-
Chlorobenzene	31.0	0.47	8.26	1700	8.05	28.6	9	0.5	0.45

	Transit from work			Home area		
	Dosimeter No. 40			Dosimeter No. 46		
	Amount collected, ng	Exp. time, hours	Concentration, ppbv	Amount collected, ng	Exp. time, hours	Concentration, ppbv
Chloroform	5.0	0.63	0.56		12.5	
1,2-Dichloroethane	1.0	0.63	-		12.5	
Carbon tetrachloride		0.63			12.5	
Trichloroethylene	6.0	0.63	0.73		12.5	
1,1,2-Trichloroethane	3.0	0.63	0.13		12.5	
Tetrachloroethylene	3.0	0.63	0.13	0.9	12.5	-
Chlorobenzene	92.0	0.63	18.1		12.5	

[a]Field blank.

TABLE 19. 1,2-DICHLOROETHANE SAMPLING WITH CHARCOAL TUBES AND PASSIVE MONITORS

Parameter	Charcoal tube No. 1	2	3	4
Flow rate, mL/min	47.2	46.2	50.2	49.0
Amount collected, µg	81	456	305	17,865
Exposure time, hr	5.6	5.6	5.6	5.6
Concentration,				
µg/L	5.1	27.8	18.2	1,027
ppmv	1.3	6.9	4.5	254
	Dosimeter No. 90	91	92	93
Equivalent, mL/min pump rate	30.0	30.0	30.0	30.0
Amount collected, µg	64.0	277	212	1,536
Exposure time, hr	5.6	5.6	5.6	5.6
Concentration,				
µg/L	6.3	25.9	21.0	144.0
ppmv	1.6	6.4	5.2	35.6

TABLE 20. WORK STATION SAMPLING STUDIES

Compound	Dosimeter sample interval[a]						Dosimeter 5-hr exposure
	1 hr	2 hr	3 hr	4 hr	5 hr	Σ	
Passive dosimeter							
Chloroform	-	-	-	-	-	-	-
1,2-Dichloroethane	0.27	0.29	0.24	0.20	~0.10	~1.1	0.67
Carbon tetrachloride	-	-	-	-	-	-	-
Trichloroethylene	0.58	0.38	0.25	0.11	0.16	1.48	1.47
1,1,2-Trichloroethane	0.16	0.48	-	0.38	0.48	1.50	0.90
Tetrachloroethylene	0.25	0.38	-	0.15	0.12	0.90	0.66
Chlorobenzene	8.4	18.2	10.4	8.6	6.7	51.0	51.0
Pumped tube							
Chloroform	-		-		-		
1,2-Dichloroethane	0.34		0.14		0.13		
Carbon tetrachloride	-		-		-		
Trichloroethylene	0.43		0.22		0.15		
1,1,2-Trichloroethane	0.49		-		0.59		
Tetrachloroethylene	0.11		-		0.17		
Chlorobenzene	7.5		9.6		5.4		

[a]Two dosimeters were spiked with chlorobenzene to determine recovery. One dosimeter was left unexposed while the second was exposed for 1 hr at the 6-hr interval under sampling conditions as above.

Exposed dosimeter	= 41.8 ppb
Unexposed dosimeter	= 35.9 ppb
Net chlorobenzene sampled	= 5.9 ppb

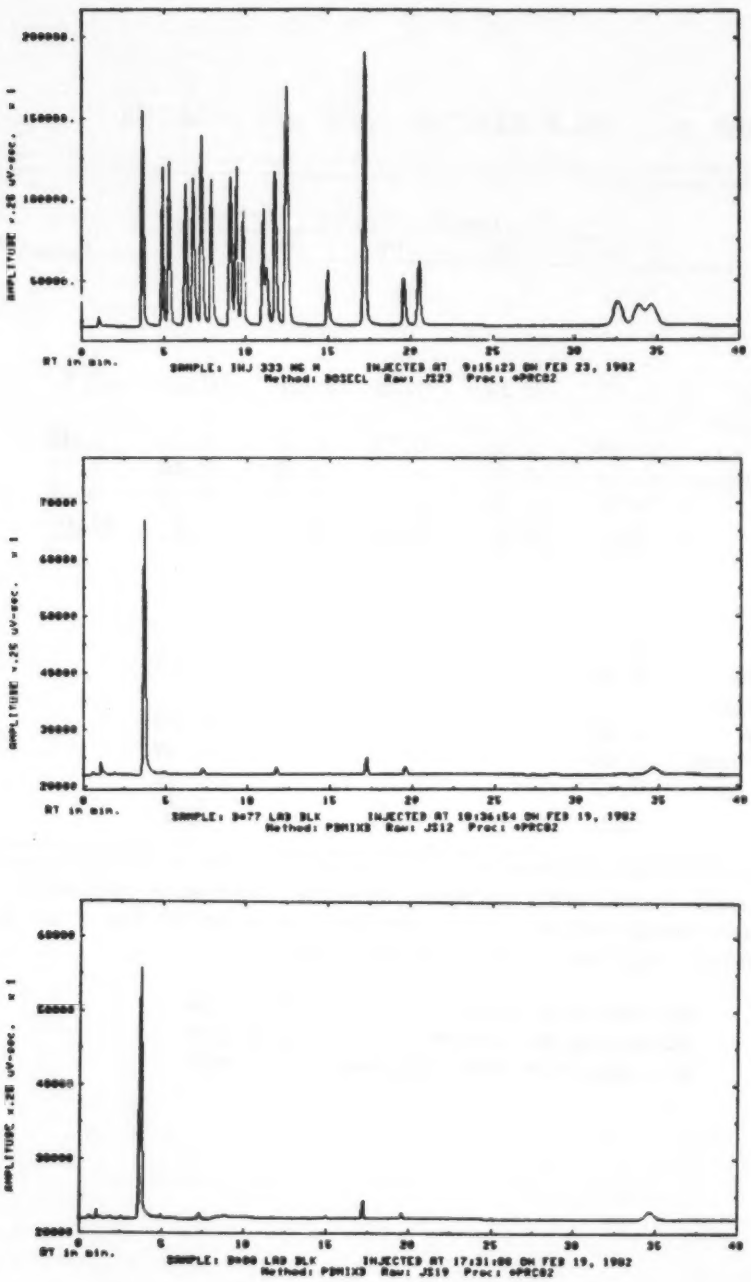


Figure 25. Reconstructed dosimeter chromatograms for EPA laboratory exposure study.

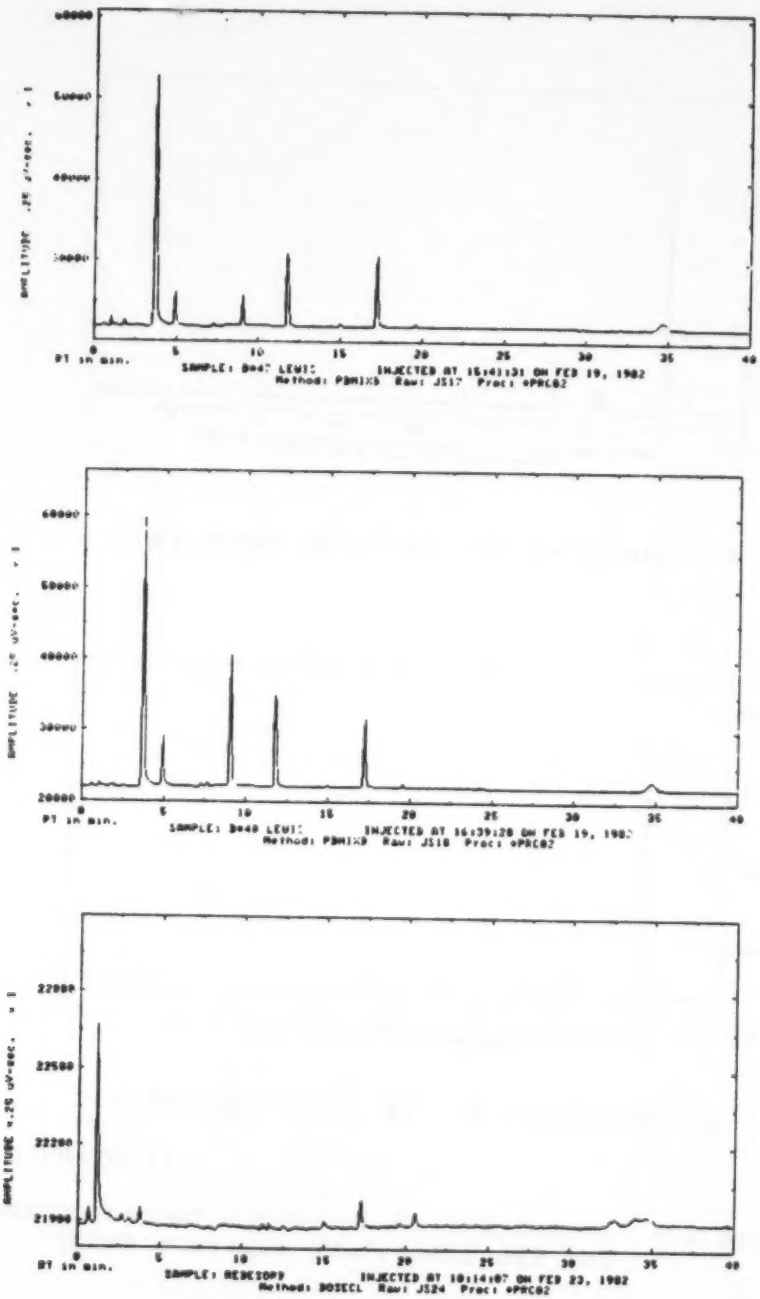
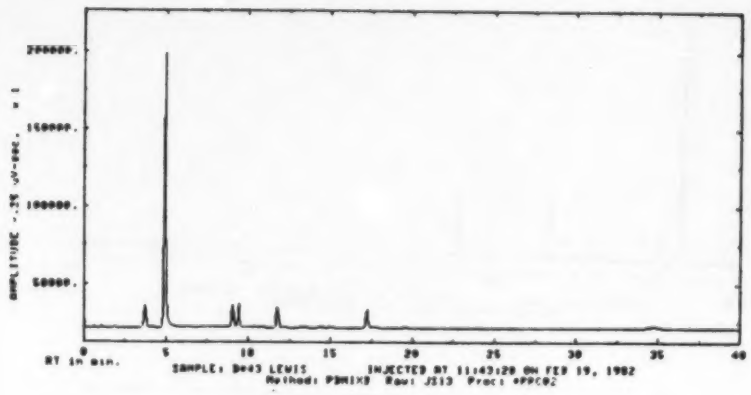
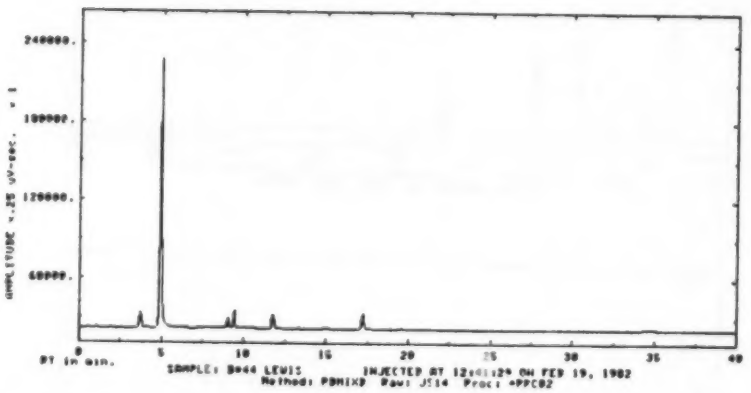


Figure 26. Reconstructed dosimeter chromatograms for EPA laboratory exposure study.



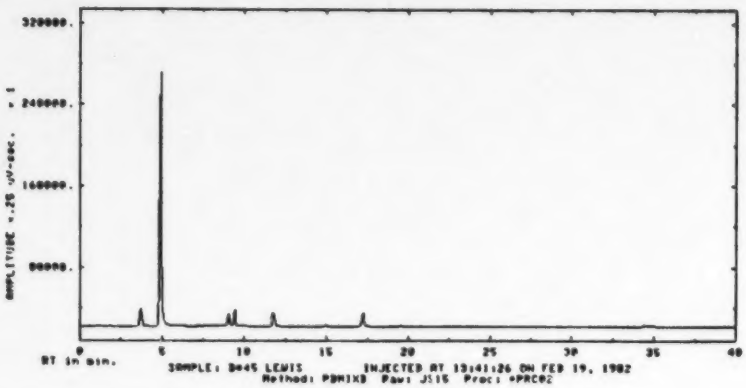
a. Dosimeter No. 43 (2-hr exposure).



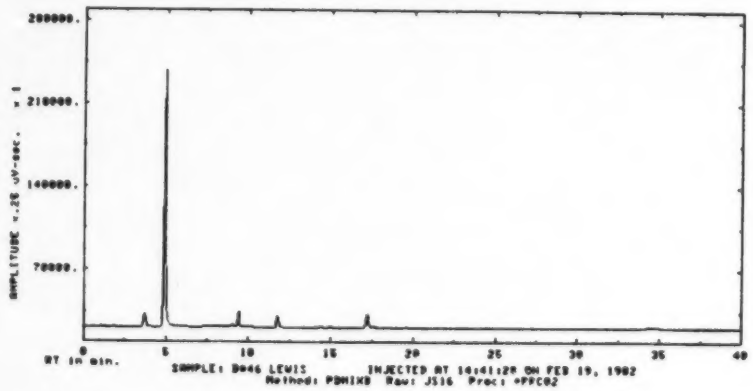
a. Dosimeter No. 44 (2-hr exposure).

(continued)

Figure 27. Reconstructed dosimeter chromatograms for EPA laboratory exposure study.



a. Dosimeter No. 45 (2-hr exposure).



a. Dosimeter No. 46 (2-hr exposure).

Figure 27 (continued)